MODELING AND SIMULATION OF HYDROCRACKING AND HYDROTREATING PROCESSES

A Thesis Submitted
in Partial Fulfilment of the Requirements
for the Degree of

DOCTOR OF PHILOSOPHY

by

Ms. SWATI MOHANTY

to the

DEPARTMENT OF CHEMICAL ENGINEERING

INDIAN INSTITUTE OF TECHNOLOGY, KANPUR

JUNE, 1989
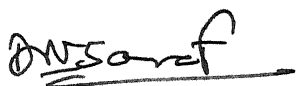
to my parents

for their encouragement

CERTIFICATE

It is certified that this work, "MODELING AND SIMULATION OF HYDROCRACKING AND HYDROTREATING PROCESSES ", by Swati Mohanty, has been carried out under our supervision and that this work has not been submitted elsewhere for a degree.

(Dr. D.N. Saraf)

Professor

Dept. of Chemical Engg.

IIT Kanpur

(Dr. D. Kunzru)

Professor

Dept. of Chemical Engg.

IIT Kanpur

June, 1989

ACKNOWLEDGEMENT

It is my distinct privilege to have got an opportunity to work under the guidance of Prof. D.N. Saraf and Prof. D. Kunzru whose inspiration and encouragement has been instrumental in getting this work completed. I express my sincere thanks to them for all the help rendered towards me and for their valuable suggestions and critical comments at various stages of the work.

I express my special thanks to Prof. Y.V.C. Rao, Prof. D.P. Rao, Prof. R.P.Singh, Prof. A.B.L. Agarwal and Prof. M.S. Rao for their helpful suggestions.

I am indebted to Mr. D.V.R. Seshadri, Mr.V.G. Vasant Kumar and Mr. Cherian of Madras Refineries for their help and hospitality during my stay at Madras.

I am grateful to Mr. Omar Salim, Mr. Srikant Jana and Mr. Pranab Dey for all the necessary help I have received from them and to Mr. Babji and Mr. S. Ganguly, for their co-operation.

I am greatly indebted to my friends, particularly, Ms. Indira Das, Ms. Pratima Mishra and Ms. Arati Nanda for their generous help and pleasant company during the preparation of this manuscript. Lastly, I feel indebted to my dearest little friend late Ms. Arundhati Mohapatra for her lively company during her stay at Kanpur.

Help received from the staff of the Department of Chemical Engineering is deeply acknowledged.

<div align="right">Swati Mohanty</div>

CONTENTS

CHAPTER 4. MODELING OF HYDROTREATING REACTOR

CHAPTER 5. CONCLUSIONS AND RECOMMENDATIONS

LIST OF TABLES

LIST OF FIGURES

NOMENCLATURE

a	parameter in Peng-Robinson's equation of state (EOS)
A	pseudo-component in the vacuum gas oil feed or parameter in Peng-Robinson's EOS
b	parameter in Peng-Robinson's EOS
B	a parameter in the hydrocracker model for predicting the yields or a parameter in Peng-Robinson's EOS
C	a parameter in hydrocracker model for predicting the yields of butanes and lighter fractions
C_c	mass fraction of the liquid feed to be cracked
C_i	mass fraction of pseudo-component i in the liquid phase
Cp_i	heat capacity of component i, kJ/(kg)(K)
$\dot{Cp}_i$	heat capacity of component i, kJ/(kmol)(K)
Cp_m	heat capacity of a mixture, kJ/(kg)(K)
$\dot{Cp}_m$	heat capacity of a mixture, kJ/(kmol)(K)
C_s	mass fraction of sulfur in liquid phase
C_s^i	mass fraction of sulfur at the inlet of the reactor
C_s^o	mass fraction of sulfur at the exit of the reactor
F_t	volumetric flow rate, m^3/h
$f^{(0)}, f^{(1)}$	functions in the prediction of reduced vapour pressure
H_{H2}	enthalpy of hydrogen at reactor conditions, kJ/kg
H_{H2}^o	enthalpy of hydrogen at 298 K, kJ/kg
H_i	enthalpy of component i at reactor conditions, kJ/kg
$\dot{H}_i$	enthalpy of component i at reactor conditions, kJ/kmol
H_i^o	enthalpy of component i at 298 K, kJ/kg

H_i^{ex} excess enthalpy for component i, kJ/kg

$H_i^{´ex}$ excess enthalpy for component i, kJ/kmol

H_i^{idl} ideal gas enthalpy of component i at reactor temperature, kJ/kg

$H_i^{´idl}$ ideal gas enthalpy at reactor temperature, kJ/kmol

$H_m^{´}$ enthalpy of the mixture at reactor conditions, kJ/kmol

H_m^{ex} excess enthalpy of a mixture, kJ/kg

$H_m^{´ex}$ excess enthalpy of a mixture, kJ/kmol

H_m^{idl} ideal gas enthalpy of a mixture at reactor temperature, kJ/kg

$H_m^{´idl}$ ideal gas enthalpy of a mixture at reactor temperature, kJ/kmol

$(H_2C)_j$ hydrogen consumption per unit mass of product for jth reaction, kg

$(H_2CR)_j$ hydrogen consumption per unit mass of hydrocarbon undergoing cracking for jth reaction, kg

HCON   overall hydrogen consumption in the reactor, kg/h

$(\Delta H_R^o)_j$ standard heat of reaction for the jth reaction, kJ/kg hydrocarbon reactant

$(\Delta H_R^T)_j$ heat of reaction at reactor conditions for the jth reaction, kJ/kg hydrocarbon reactant

$(\Delta H_R)_c$ heat of reaction for the hydrocracking reaction, kJ/kg hydrocarbon reactant

$(\Delta H_R)_c^{´}$ molar heat of reaction for the hydrocracking reaction, kJ/kmol hydrocarbon reactant

$(\Delta H_R)_s$ heat of reaction for the HDS reaction, kJ/kg S reacting

$(\Delta H_R)_s^{´}$ molar heat of reaction for the HDS reaction, kJ/kmol S reacting

k   rate constant for the reference pseudo-component, (kg feed)/(kg cat.)(h)

k_i rate constant for the ith pseudo-component, (kg feed)/(kg cat.)(h)

k_c — rate constant for the hydrocracking reaction, (kg feed)/(kg cat.)(h) or (kmol feed)/(kg cat.)(h)

k_s — rate constant for the HDS reaction, $\dfrac{(\text{kg feed})^2}{(\text{kg cat.})(\text{kg S})(h)}$ or $\dfrac{(\text{kmol feed})^2}{(\text{kg cat.})(\text{kmol S})(h)}$

k_{ij} — binary interaction parameter for Peng-Robinson's EOS

K_i' — relative rate constant for the ith component

K_i — vapour-liquid equilibrium constant for component i

M_t — mass flow rate, kg/h

m_i — component mass flow rate, kg/h

$(MW)_i$ — molecular weight of component i

m_i' — component mass flow rate at the inlet of the reactor, kg/h

m_i'' — component mass flow rate at the exit of the reactor, kg/h

n_i — molar flow rate of component i, kmol/h

N — total number of pseudo-components

$N1$ — total number of components in a gas mixture

N_t — total molar flow rate, kmol/h

N_t^i — total molar flow rate at the inlet of the reactor, kmol /h

N_t^o — total molar flow rate at the exit of the reactor, kmol/h

N_{tl} — liquid molar flow rate, kmol/h

N_{tl}^i — liquid molar flow rate at the inlet of the reactor, kmol/h

N_{tl}^o — liquid molar flow rate at the exit of the reactor, kmol/h

N_{tv} — vapour molar flow rate, kmol/h

P_{ij} — probability of ith pseudo-component being formed from jth pseudo-component

P'_{ij} cumulative yield till the ith pseudo-component formed fro jth pseudo-component

P_{ci}, P'_{ci} critical pressure of the ith component, atm., psi

Pvp_i vapour pressure of component i at reactor conditions, atm.

Pvp_{ri} reduced vapour pressure of component i at reactor conditions

P_T reactor pressure, atm

R universal gas constant, $(m^3)(atm)/(kmol)(K)$ or

       $kJ/(kmol)(K)$

R'_j carbon-to-hydrogen ratio for the jth pseudo-component

SG_i specific gravity of ith pseudo-component

t temperature in ^oC

t' temperature in ^oF

tb_j boiling point of the component j, ^oC

Tb_j boiling point of the component j, K

T_{ci} critical temperature of component i, K

T_{br} reduced boiling point of component i

T_{cm} critical temperature of a mixture, K

$(TWC)_j$ carbon content of the products formed during cracking of jth component (jth reaction), kg

$(TWH)_j$ hydrogen content of the products formed during cracking of jth component (jth reaction), kg

$(TR)_j$ total weight of pseudo-component j which would give unit mass of product in the jth reaction, kg

V_{ci} critical volume of component i, $cm^3/gmol$

V_{cm} critical volume of the mixture, $cm^3/gmol$

W weight of the catalyst bed, kg

$W'_{c.j}$ carbon content in $(TR)_j$ kg of pseudo-component j, kg

$W_{H2,j}$ hydrogen content in $(TR)_j$ kg of pseudo-component j, kg

x_i mole fraction of component i

x_i' mole fraction of component i in the liquid phase

x_c' mole fraction of the uncracked feed in the liquid phase

x_s' mole fraction of sulfur in the liquid phase

y_i' mole fraction of component i in the vapour phase

y_{ij} normalised temperature for the ith pseudo-component formed from jth pseudo-component in the jth reaction

z_i' mole fraction of componemt i in the reaction mixture to be flashed

Z compressibility factor

Z_{ci} critical compressibility factor

GREEK SYMBOLS

ω_i acentric factor of component i

$\varnothing$ fugacity co-efficient

α parameter in Peng-Robinson's EOS

$\hat{\varnothing}_i$ partial fugacity co-efficient of component i

ρ_i density of component i, gm/ml

$\hat{\varnothing}_{iL}$ partial fugacity co-efficient of component i in the liquid phase

$\hat{\varnothing}_{iV}$ partial fugacity co-efficient of component i in vapour phase

θ surface fraction

SYNOPSIS

Hydrocracking and hydrotreating are some of the major refinery processes carried out for upgrading of petroleum crude and its fractions. With increasing demand for light and middle distillates and continued depletion of petroleum resources, the need to crack heavy oils and residues is increasing. Hydrocracking is practised in most of the modern refineries for production of lighter fuels. It is a very versatile process and can be used to crack a wide variety of feedstocks ranging from naphtha to heavy residues. The most commonly used catalyst is $CoMo/Al_2O_3$. To date, only a few models for hydrocracking reactors have been reported and these reveal very few details. Cracking consists of several parallel and consecutive reactions. Product distribution during hydrocracking of n-paraffins has been reported by several authors but no experimental results are available for cracking of petroleum fractions.

In the present work, a model for a two-stage vacuum gas oil hydrocracker unit has been developed. The first stage consists of four beds and the second stage consists of three beds of catalyst with intermediate quenching. The products from the first stage are fractionated and only those boiling above 643 K are recycled to the second stage. The effluent from the second stage is also fractionated and the heavier fractions recycled to the second stage. For the modeling, the feed was lumped into 23

pseudo-components with a specified boiling range interval of 25K
The product distribution was obtained using empirical correlation
assuming that only those fractions having boiling point above 400
undergo cracking. The model assumes that the lightest produc
formed has boiling point of 275.5K (ie. an average boiling poin
for butanes and lighter fractions) and the heaviest product forme
has a boiling point 50K lower than that of the fraction from whic
it is formed. The molecular weight and the critical properties o
the pseudo-components were estimated using the Lee-Kesler'
correlation and the enthalpies predicted based on Peng-Robinson'
equation of state. As suggested by several authors, a first orde
rate constant was assumed for each component. To simplify th
model, power law, rather than Langmuir- Hinshelwood, type of rat
expression was used. Carbon-to-hydrogen ratio data available fro
the published literature were used to calculate the heats o
reaction. Altogether 17 parallel reactions were considered.

The differential mass and energy balance equation
forming the mathematical model were solved using the fourth orde
Runge-Kutta-Gill method. The yields of various products such a
the butanes and lower fractions, naphtha, aviation turbine fue
and high speed diesel as predicted by the model were in goo
agreement with the available data. The reactor temperature at th
exit of each bed could not be compared as only the maximu
temperature at the outlet was available.

Hydrodesulfurisation is also an important process whe
crudes or petroleum fractions containing high percentage of sulfu
are to be processed. Sulfur compounds not only poison the cataly
but also have a deleterious effect on refining equipment a

impart undesirable characteristics to the refined products. Along with sulfur compounds, small amounts of nitrogen and oxygen compounds present in the crude or petroleum fractions may also be removed and the aromatics saturated. Such a process is termed as hydrotreating. Sulfur is removed in the form of hydrogen sulfide and nitrogen as ammonia. $CoMo/Al_2O_3$ is the most commonly used catalyst. The chemistry and kinetics for hydrodesulfurisation are generally available for pure sulfur compounds with thiophene, benzothiophene being the most common model compounds. Several commercial and patented processes are available. The process is generally carried out in a single stage fixed bed reactor with or without intermediate quenching.

In the present work, models for three hydrodesulfurisation units processing three different feedstocks are developed: (i) vacuum distillate (ii) kerosene (iii) diesel. The petroleum feed in the case of vacuum distillate was in the liquid phase, vapour phase in the case of kerosene and was partially vapourised in the case of diesel feed. As in the case of hydrocracking model, the feed was divided into pseudo-components for estimating the enthalpies, but due to lack of kinetic data the total sulfur present in the feed was represented by a single model compound.

For the vacuum distillate hydrotreating model, the representative sulfur compound chosen was substituted dibenzothiophene. The products formed are substituted cyclohexyl benzene and substituted biphenyl along with hydrogen sulfide. Although for pure sulfur compounds first-order kinetics have been reported the hydrodesulfurisation of petroleum fractions is

generally represented by second order kinetics. All calculations were done on a mass , rather than mole basis. The liquid and mass flow rates were assumed to be constant.

For kerosene desulfurisation, the model sulfur compound chosen was tri-subtituted thiophene. Although the aromatic content of the kerosene was high (22 vol. %), plant data revealed that the aromatic saturation was negligible, presumably due to milder reaction conditions. A second order power law expression was assumed. Since the entire feed was in the vapour phase, the concentrations were expressed in terms of partial pressures and the calculations performed on a molar basis.

The diesel feed was in a partially vapourised state; hence vapour-liquid equilibrium data were used to predict the concentrations of the vapour and liquid phases. Ideal K values were used for the petroleum fractions and a suitable K value was assumed for hydrogen as no reliable vapour-liquid equilibrium correlations are available for petroleum fractions containing hydrogen. The vapour pressures were predicted using the Lee-Kesler's modification of Pitzer equation. Benzothiophene was chosen as the model compound and a second order rate constant was assumed. All calculations were done on molar basis.

The differential mass and energy balance equations for hydrotreating processes were solved using the Runge-Kutta-Gill method. The models were used to predict the sulfur concentration at the exit of the reactor, the hydrogen consumption and the reactor exit temperature. The actual temperature at the exit of the reactor was not available except for the design data. Hence the only data which could be compared in the case of operating

data set was the exit sulfur concentration. The sensitivity of temperature and the sulfur concentration in feed on the reactor performance was studied. The exit reactor temperature was not affected significantly by a change in the reactor inlet temperature. In general the exit sulfur concentration decreased with an increase in the reactor inlet temperature. An increase in the sulfur concentration resulted in an increase in the reactor outlet temperature.

The hydrocracking and hydrotreating models developed in this study can be used for rating of similar other units as well as for optimization of plant operating conditions. These models after suitable modifications, can also be used for design of new plants.

CHAPTER - 1

INTRODUCTION

Hydrocracking and hydrotreating processes find extensive application in petroleum refineries. The hydrocracking process was developed commercially by I.G. Farben industries in 1927 for converting lignite into gasoline (Gary and Handwerk, 1975). This process did not find widespread application because of the high cost of manufacturing hydrogen. With the introduction of catalytic reforming in the early fifties, hydrogen became available at a nominal cost, and hydrocracking became an attractive alternative for upgrading of heavy petroleum fractions. Since the introduction of modern hydrocracking to the industry in 1959, the worldwide hydrocracking capacity has increased steadily. In 1983 there were around 126 commercial installations including those under construction with a capacity of 2.5×10^5 m^3 oil per day (Yan, 1983). Since the platinum catalysts used for catalytic reforming are very sensitive to sulfur poisoning, it became necessary to desulfurise the naphtha feedstocks to these units. Thus hydrodesulfurisation became an important refining process in the 1950's, and has been gaining importance ever since. The first commercial desulfurisers were used to clean naphthas but by 1960's, desulfurisation of other feedstocks such as kerosene, diesel and vacuum gas oils became important and in the 1970's

desulfurisation of residual oil was also introduced. This led to the development of widely used hydrotreating processes.

Both, hydrocracking and hydrotreating processes are carried out in fixed bed catalytic reactors in the presence of hydrogen under pressure. There are a large number of commercial processes and patents available. Various types of catalysts such as cobalt-molybdenum or nickel-tungsten supported on silica-alumina or zeolites are used in these processes. Several kinetic studies are also available although these are either for hydrodesulfurisation (HDS) of pure sulfur compounds or hydrocracking of pure n-paraffins. However, very limited research has been done on the modeling of these reactors. The available models reveal very little details and do not provide any insight into the process.

In the present study reactor models for these two processes have been developed. For hydrocracking, the feedstock was vacuum gas oil which was subdivided into a number of pseudo-components and the mass and energy balance equations written for each pseudo-component. The model parameters were taken from published information or estimated from plant data. Models have been developed for hydrotreating of various feedstocks such as vacuum distillate, kerosene and diesel. In view of the non-availability of detailed distribution of sulfur compounds in the feedstocks, the entire sulfur was represented by a model compound. These models were validated against available plant data. The major use of such models is in the optimization of existing units and in the design of new reactors. For instance, the models can be used for predicting the reactor performance under different conditions so as to arrive at optimum conditions.

The model can also be used to simulate conditions which are too dangerous to attempt on a real plant. With the general trend in modern industries to solve problems analytically, such models may find industrial applications in petroleum refineries.

The thesis is presented in five chapters. The available information on the technology, kinetics, chemistry and reactor modeling of these processes is summarised in Chapter 2. The development of the model for hydrocracking together with its application and validation against plant data is presented in Chapter 3. The models for hydrotreating units are given in Chapter 4. In the same chapter, sensitivity of the process paramaters is also discussed. The conclusions and suggestions for further work are summarised in Chapter 5.

REFERENCES

Gary, J.H.; Handwerk, G.E. "Petroleum Refining : Technology and Economics" Marcel Dekker, Inc., New York, 1975.

Yan, Y.Y. "Zeolite-Based Catalyst for Hydrocracking" Ind. Eng. Chem. Process Des. Dev., 22, 154-160, 1983.

CHAPTER - 2

LITERATURE REVIEW

2.1 HYDROCRACKING

Hydrocracking is practised in modern petroleum refineries for converting various higher boiling range hydrocarbons into more valuable products such as gasoline, diesel and jet fuel (Yan, 1980). Even though product projections show decreasing demand for gasoline and increasing demand for middle distillates, gasoline remains the most important product in the U.S. . Hydrocracking is a highly flexible petroleum refining process which can take feedstocks ranging from light naphthas to deasphalted vacuum residue (Sikonia et al., 1981). Other applications of this process includes upgrading of petrochemical feedstocks (Mavity et al., 1978), improvement of gasoline octane number (Chen et al., 1968) and production of high quality lubricants. In addition, very heavy hydrocarbon deposits such as tar sands, shale oil etc. can be upgraded by hydrocracking (Friz et al. 1983). The process upgrades the original stock by increasing its overall hydrogen to carbon ratio and decreasing the average relative molecular mass.

Depending upon the end product required, the operating conditions and catalysts for hydrocracking may vary. The progress of hydrocracking process has largely depended on the development of catalysts with improved activity and selectivity. Earlier,

unsupported tungsten sulfide was used as a presaturation catalyst but with subsequent development, it was replaced by supported catalysts such as nickle-tungsten sulfide on alumina and cobalt molybdate on alumina. These changes contributed to the production of aromatic gasoline of higher octane number (Voorhies and Smith, 1964). All hydrocracking catalysts are dual functional (Steijns et al., 1981; Vansina et al., 1983). The catalyst consists of hydrogenation metal(s) on an acidic cracking base. Commonly used hydrogenation components include cobalt, molybdenum, tungsten, nickel, platinum and palladium. The cracking component is an acidic carrier which may be amorphous silica-alumina of various compositions, or crystalline carriers such as cation exchanged faujasites X and Y (Ward et al., 1973). In a hydrocracking process, the liquid yield is about 10-15 mass percent higher than that for delayed coking process, which is desirable.

Recently, a new technology known as mild hydrocracking has been introduced. The advantage of this technology is that it can use existing hydrotreaters for hydrocracking by increasing the severity of operation. The product is mainly middle distillate which is an excellent quality diesel oil blendstock. The process is steadily gaining importance with 76% of the units in Japan and 42% in Western Europe practising this technique at present (Sonnemans et al., 1984). Recent developments made in the hydrocracking processes have been reviewed by Chowdhary and Saraf, 1975; Maxwell, 1983 and Fritz et al. 1983.

2.1.1 Processes

A wide variety of feedstocks ranging from light naphthas to residual oil can be hydrocracked to obtain lighter products.

One, two or more stages may be required depending on the nature of the feedstock used and the end products desired. A typical two-stage hydrocracker is shown in Figure 2.1. The first stage acts as a hydrotreater which removes poisonous nitrogen compounds and improves the quality of the feed entering the hydrocracker. The product from the first stage reactor is passed through a high pressure separator before it is fed to the second stage reactor. In the second stage, the hydrotreated feed is hydrocracked to gasoline and/or kerosene, and lighter products. The products pass through a high pressure separator and then to a distillation tower where the unconverted feed is separated and recycled along with fresh pretreated feed into the second stage for further cracking (Yan, 1983). This mode of operation is known as extinction recycle hydrocracking. There is no purge stream to remove the refractory compounds present in the feed and hence the severity of the processs has to be increased to enforce the conversion. A hydrocracker reactor generally operates at a temperature range 530 to 700 K and pressure 6.5 to 13.5 MPa. Except for the H-oil and Hy-C processes, which were codeveloped by Cities Service Research and Development Company and Hydrocarbon Research, Incorporated, others use fixed-bed reactors with liquid downflow (Gary and Handwerk, 1975; Yan, 1983). The details of the reaction conditions and product yields for the major commercial hydrocracking processes are available in Refining Process Handbook, 1986.

In addition to these processes, several other investigations on hydrocracking have been reported. Sikonia et al. (1981) developed a process which can hydrocrack any fraction from naphtha to demetallised oil (DMO) to yield desired products. During hydrocracking, most of the sulfur, nitrogen and oxygen were
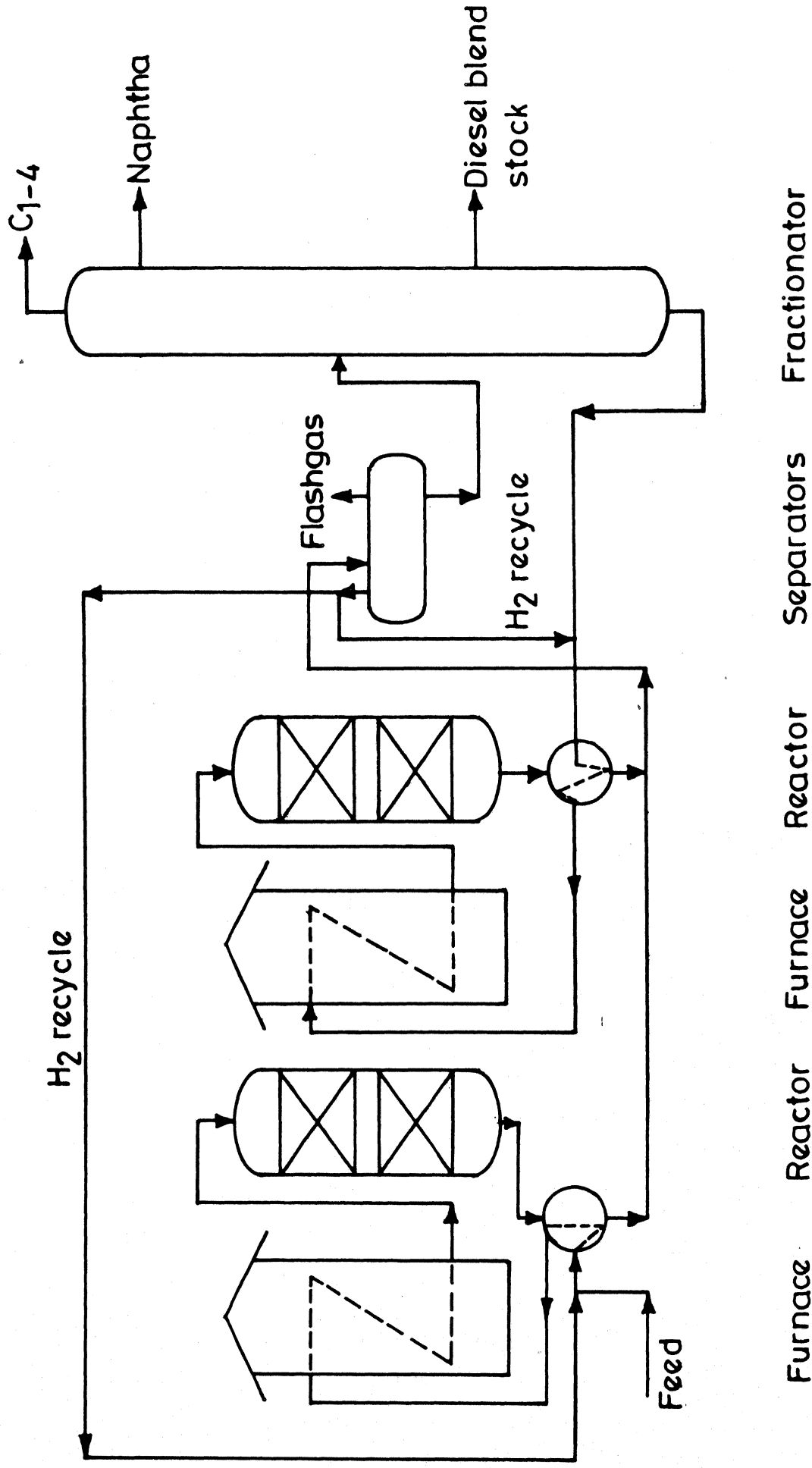
Fig.2.)- A schematic diagram of a hydrocracking process.

removed and the olefins saturated so that the product obtained was a mixture of pure paraffins, naphthenes and aromatics. The catalysts were so chosen that these were selective to producing distillate products. The process can be carried out in a single stage, two stage or series flow to meet various objectives of hydrocracking. A higher octane gasoline was obtained by first reforming a 335-453 K gasoline followed by hydrocracking. For 358-453 K straight run gasoline, hydrocracking was not required as the octane number was 99.5 by reforming alone (Shipikin et al., 1983).

Nasution (1983) obtained optimum yields of middle distillates by subjecting Kuwait vacuum distillates to hydrocracking at 0.88 h^{-1} space velocity, 683 K temperature, hydrogen to feed volume ratio of 1000:1 and at a pressure of 10 MPa. The catalyst used was Co-Mo/Al_2O_3. Radchenko et al. (1983) used a two-stage process for hydrocracking of vacuum distillate. In the first stage a desulfurising catalyst, Ni-Mo/Al_2O_3 was used and in the second stage Mg silicate catalyst was employed. The products were winter diesel and jet fuel when the operating pressures were 10 and 15 MPa, respectively. When a vacuum distillate was subjected to hydrocracking at 605-645 K and 11 MPa pressure over a zeolite catalyst containing Co-Ni, the main products were C_3H_8 and C_4H_{10} (Kotowski and Benbenek, 1981).

Hydrocracking of residual oils obtained from vacuum or atmospheric distillation of various crudes was carried out by Sakabe and Yagi (1979) and Ukegawa et al. (1980) by using spent catalyst from a desulfurisation unit. Kotowski (1982) investigated the hydrocracking of a deasphalted and demetalated atmospheric residue of Ramashkino crude in a 3-phase dynamic reactor at

temperature 685-705 K and catalyst concentration 7-9 wt.%. The yield of fuel oil decreased with increasing flow rate.

A review on hydrocracking of light Arabian vacuum gas oil over a zeolite catalyst for maximum conversion to middle distillates is given by Light et al. (1981). Sasaki et al. (1983b) hydrocracked a high metal content heavy oil over an aqueous vanadyl oxalate catalyst at 715 K, 10 MPa hydrogen pressure, oil feed rate 0.001 m^3/h and stirring rate 950 rpm. A two-stage hydrocracking process carried out by Kotowski (1983) consisted of first thermal treating a mixture of coal and heavy oil so as to aromatise the fuel oil and depolymerise the coal and then catalytically hydrocracking in two stages to give C_1-C_4 gases, naphtha, diesel oil and fuel oil. A sour crude was first diluted with recycle oil and then hydrocracked over a fixed bed of Ni-Mo/Al_2O_3 catalyst at 725 K, 3 MPa and 2 h^{-1} space velocity by Katsobashvili and Teplyakova (1984) and the products obtained were gasoline, diesel fuel and fuel oil. Schuetze and Hofmann (1984) described several other processes such as Aurabon, ABC, Residue HC, M-coke and VEBA which have been tested at pilot-plant scale.

Mild hydrocracking process which is gaining importance in recent years has been discussed by a number of authors (Gembicki et al., 1983; Jaeckh et al., 1984; Sonnemans et al., 1984). These workers used existing vacuum gas oil desulfuriser for conversion of vacuum gas oil to middle distillates. In the study of Sonneman's et al. the conversion was about 36 percent at operating pressures below 7 MPa. Middle distillate formed was about 26 vol. percent of feed, heavy naphtha, 2.3 vol. percent and lighter products, 2 wt. percent.

2.1.2 Chemistry

Although there are a number of reactions taking place simultaneously during hydrocracking, the mechanism of hydrocracking is similar to that of catalytic cracking with hydrogenation superimposed. The catalyst activity is maintained at a high level because of lower coke deposition. With a sulfided nickel supported on a silica-alumina catalyst, excessive splitting produces large amounts of low-molecular weight paraffins with a high iso/normal ratio. Platinum on silica-alumina, which has a much higher hydrogenation activity, gives more of intermediate than low molecular weight paraffins thus minimising the ratio of gas to liquid products. With a more active hydrogenation catalyst such as metallic nickel and platinum, the ratio of iso/normal light paraffin may be low. The product distribution for some n-paraffins over zeolite catalyst is given by Steijns et al. (1981) and Vansina et al. (1983). Olefins are more readily hydrocracked than paraffins (Voorhies and Smith, 1964). It is seen that cracking reaction is endothermic whereas hydrogenation reaction is exothermic. Since the heat required for cracking is less than the heat released during exothermic reaction, the temperature is maintained by injecting cold hydrogen into the reactor. Generally hydrocracking reactions take place at temperatures between 560-690 K and pressures between 8 to 13.6 MPa (Gary and Handwerk, 1975). Before cracking, both intermolecular and intramolecular rearrangements take place which do not permit prediction of final product spectrum obtainable from a given feed. With nonacidic or weakly acidic catalysts, the reactions are generally less complex and take place on the hydrogenating component. Very little isomerisation or structural rearrangements

take place and the reaction products are generally simple fragments of the original reactant. By using a catalyst which is intermediate between acidic and nonacidic, cracking occurs both on the acidic component and hydrogenation component and the products are also intermediate in character (Voorhies and Smith, 1964). Langlois and Sullivan (1970) reviewed the chemistry of catalytic hydrocracking of hydrocarbons in detail. The available information indicates that hydrocracking of normal paraffins involves scission of the carbon- carbon bond at different sites. For instance, the products from the hydrocracking of n-decane can be represented as follows:

$$C_{10} \longrightarrow
\begin{cases}
C_5 + C_5 \\
C_6 + C_4 \\
C_7 + C_3
\end{cases}$$
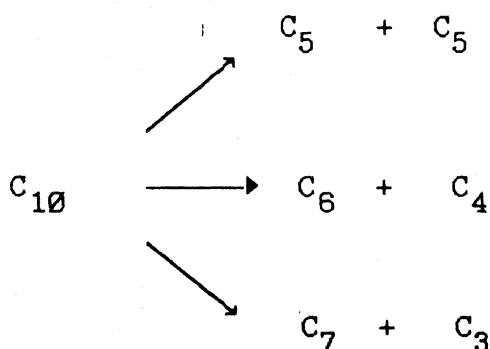
The amounts of C_3 and lighter paraffins is generally negligible. The normal paraffins formed during the cracking step can also be converted to isoparaffins by hydroisomerisation. The proportion of the normal to iso-paraffins depends on various factors such as the acidity of the catalyst, conversion level, temperature etc. When normal paraffins are hydrocracked over a strongly acidic catalyst, the products consist mainly of iso-paraffins and small amounts of n-paraffins are isomerized without cracking (Langlois and Sullivan, 1970). Other studies on the reactions of hydrocracking of paraffins have been carried out by Archibald et al. (1960), Flinn et al. (1960), Coondart and Garwood (1964), El-Kady et

al.(1983a), Rabinovch et al. (1983), Panchenkov et al. (1983) and Goldfarb et al. (1981). Reactions of cycloparaffins over strongly acidic catalysts were studied by Egan et al. (1962). On hydrocracking alkyl aromatics with side chains on a strongly acidic catalyst, paraffins and benzene were produced (Sullivan et al., 1964). They also studied complex reactions of polycyclic aromatics over acidic hydrocracking catalysts. Schneider et al. (1981) studied the hydrocracking reactions of petroleum vacuum distillate. From spectroscopic analysis, chromatographic separation and structure analysis of products, they concluded that the aromatic ring hydrogenation and cleavage are the main reactions involved.

2.1.3 Catalysts

Type of catalyst varies with the feedstock being processed. $CoO-MoO_3-Al_2O_3$ has been widely used for hydrocracking of heavy feedstocks such as residual raffinate, solvent deasphalted residual oil and vacuum residue (Kondo et al., 1982; Nasution, 1983; Chesnokov et al.,1985). The catalyst activity decreases and selectivity changes with age and more gas than naphtha is produced as the catalyst temperature is raised to maintain conversion. Regeneration is necessary when the catalyst poisoning due to deposition of coke and other materials reaches a certain level. This is usually accomplished by burning off the catalyst deposits. Kelly and Ternan (1979) studied the activity of $CoO-MoO_3-Al_2O_3$ catalyst promoted with sodium, potassium or lithium. Lithium showed the best result as regards conversion and pitch, oxygen, sulfur and nitogen removal.

Ni-Mo, Ni-W and Ni-Co have also been used as

hydrocracking catalysts. El-Kady, 1979; Jaeckh et al., 1984; Nasution, 1985 employed Mo-Ni/SiO$_2$-Al$_2$O$_3$ catalyst for hydrocracking of vacuum distillates. Katsobashvili and Teplyakova (1984) used the same metals on alumina for hydrocracking of a sour crude. Impregnating V and one of the metals from Zn, Fe, Co, Ni, Cu, Ag, Sn or Pb on an Al$_2$O$_3$ or TiO$_2$ support has been found suitable for hydrocracking of petroleum atmospheric and vacuum residues (Togari et al., 1983). Ghosal (1985) hydrocracked straight run vacuum gas oil on a Ni-Mo on zeolite Y catalyst containing rare earth elements. Yan (1983) developed a new dual catalyst, NiW/REX-Ni/SiO$_2$-Al$_2$O$_3$ for extinction hydrocracking. The Ni-W impregnated on rare earth exchanged X-type catalyst was found to be more nitrogen resistant, more selective to desirable naphtha product and was more stable in structure whereas Ni/SiO$_2$Al$_2$O$_3$ helped in the extent of conversion of heavy, polynuclear compounds in the feed. The catalyst can be used for hydrocracking heavy feeds of wide boiling range. LaX and NiX catalysts were used for the hydrocracking of Assam crude by Choudhary and Saraf (1978). They reported that NiX had a lower activity than LaX. Kotowski (1981) used Co-Ni catalyst on zeolite Y carrier for hydrocracking of vacuum distillates. Swift and Black (1974) studied the activity of synthetic mica-montmorillonite with Ni or Co incorporated into the lattice structure. The activity was found to be greater than that obtained from Pd-rare earth-Y zeolites or Pd-H-modernite.

Tests carried out by Kondo et al. (1984) on hydrocracking of heavy oil from different sources showed that Ni-V/Al$_2$O$_3$ catalyst was more active than either Co-Mo or Ni-Mo, and spent catalyst from a desulfurisation unit can be used for hydrocracking. Aqueous vanadyl oxalate prepared from V$_2$O$_5$ and

$(CO_2H)_2$ (1:4 mole ratio) was found to be very effective for hydrocracking heavy oils with high metal content (Sasaki et al., 1983b). Sasaki et al (1983a) prepared a catalyst from heavy oil known as Ash Catalyst and used it for hydrocacking of heavy oils. It was green-yellow in colour with a high vanadium content. Though the activity of this catalyst was lower than that of $Co-Mo/Al_2O_3$, it produced the same level of liquid products as the latter. Coke formation decreased whereas metal removal increased with an increase in the amount of Ash Catalyst. Katowski (1983) used coal as a catalyst for hydrocracking of fuel oil.

Morita et al. (1980) investigated the effect of zinc chloride catalysts supported on silica, silica-alumina and alumina on hydrocracking of anthracene. Zinc chloride supported on silica-alumina was the most active. By pretreating the catalyst, the yield of gaseous product was lowered. Franck and Page (1980) prepared a number of catalysts containing Ni (or Co) and Mo (or W) on silica-alumina carriers and studied their effect on various types of feedstocks. Aboul-Gheit (1987) studied the hydrocracking of VGO on $NiMo/Al_2O_3-SiO_2$-zeolite HY catalysts.

2.1.4 Kinetics

Hydrocracking of petroleum feed stocks proceed through a network of complex reactions involving a large number of components which makes the kinetic study of these reactions extremely difficult. For simplification, the reaction steps and products are lumped into groups. Some of the kinetic models developed have been reviewed by Sue and Sugiyama (1982). Steinberg et al. (1985) have given an overview of the research and development work carried out at the Leuna, East Germany

petrochemical complex on hydrocracking of n-alkanes to branched alkenes over zeolite catalysts.

For hydrocracking of light hydrocarbons Bernardo and Trinun (1977) postulated a Langmuir-Hinshelwood type of kinetic model which accounted for the effect of carbon formation on a nickel catalyst. Raseev and El Kharashi (1978) studied the kinetics of naphtha hydrocracking and calculated the heat of adsorption and activation energy of the surface reactions. Arayici and Deymer (1979) studied the kinetics of hydrocracking of naphtha over $Pt/SiO_2-Al_2O_3$ with chloroform added during the process. A kinetic model for hydrocracking of middle distillate was developed by Grendele (1980). Miklena et al. (1980) studied the kinetics of hydrocracking of n-alkanes. Hydrocracking of n-decanes, n-undecanes and n-dodecanes over Pt/Al_2O_3 and $Ni \ Mo/Al_2O_3$ was investigated by Goldfarb et al.(1981). For their kinetic study, the products obtained from n-decane hydrocracking were lumped into methylnonanes, dimethyloctanes and cracked products.

Steijns and Froment (1981) developed kinetic models for hydroisomerisation and hydrocracking of n-decane, n-dodecane over zeolite catalysts. They assumed that the pores were completely filled which leads to a pseudo-zeroth order behavior and the concentration of the reacting molecules at the active sites was determined by the physical adsorption processs. The model was found to be superior to those which did not account for physical adsorption. Marin and Froment (1982) considered the possible intervention of hydrogen through a Rideal mechanism for the hydrocracking of C_6 hydrocarbons.

The kinetics of n-octane hydroisomerisation and hydrocracking over zeolite catalyst was modelled by Baltanas et

al. (1983) using the assumptions made by Steijns and Froment(1981) that the concentration of the reacting molecules at the active site is determined by the physical adsorption process. The rate of hydroisomerisation followed the same trend as that for n-decane and n-dodecane. They assumed a Langmuir-Hinshelwood mechanism for chemisorption and Langmuir isotherm for expressing the hydrocarbon concentration. Several models were developed and the discrimination between rival models was done statistically.

Kinetics of hydrocracking of n-heptane over Pt/Al_2O_3 catalyst containing various additives was studied by Sokolov and Zaidman (1983). El-Kady et al. (1983b) carried out hydroisomerisation of n-heptane over $Pt/SiO_2-Al_2O_3$ catalyst and reported that at low and/or moderate temperatures (600-675 K) the balance of cracking- hydrogenation was shifted towards more hydrogenation and at severe conditions the shift was towards more cracking. Rabinovich et al. (1983) and Panchenkov et al. (1983) studied the kinetics of hydrocracking of heptane over a polymetallic-platinum-containing reforming catalyst. The kinetics of gas oil and vacuum distillate have been studied by Qader and Hill (1969) and El-Kady (1979), respectively. These authors found the rate of hydrocracking to be first order with respect to feed concentration. Nasution (1985) made a kinetic study of hydrocracking of vacuum distillate over a $Ni-Mo/Al_2O_3-SiO_2$ catalyst for production of middle distillate. The apparent activation energy for hydrocracking was determined to be 108 MJ/kmol.

2.1.5 Reactor Modeling

Several models have been suggested for hydrocracking

reactors which are summarised below.

Jaffe (1976) developed a model which accounts for the hot spots that are generated due to the rapid reaction in the regions of low flow and the temperature drop due to mixing of cooler fluid from the surrounding region. The reactions were modeled by identifying lumped species and a kinetic model was developed accounting for the conversion of reactant lumped species to product lumped species.

Gerdes et al. (1977) developed a model for a fixed bed hydrocracker taking into consideration four classes of reactions: hydrocracking, saturation, desulfurisation and denitrogenation. The catalyst bed was divided into horizontal tanks of specified thickness. The stirred tank consisted of three regions, a solid region consisting of catalyst matrix, the pore volume and the external void space. The model assumes that as the liquid flows down, it fills the pore volume. Excess liquid flows down to the tank below by undergoing reaction and subsequent vapourisation. The external void is also filled with liquid, leaving space for vapour flow and is represented by external hold-up. The excess liquid is cascaded to the tank below. Simple phase equilibrium calculations were made and it was assumed that if the equilibrium liquid was not enough to fill the pores, these were filled by condensation of heavy hydrocarbon components. A simple kinetic model was assumed with reaction rate being proportional to the density of the reacting species and to the hydrogen partial pressure. Since under normal hydrocracking conditions, diffusional resistance is not limiting, this model has neglected it.

Yan (1977,1980) developed a model to study the dynamic behavior of an adiabatic trickle-bed reactor without and with gas

or liquid quenching. He assumed that the fluid pattern was plug flow, temperature and concentration were uniform across the cross section, heat capacities and heat of reaction of the liquid and gas were constant, reaction took place at the surface, vapour behaved as an ideal gas and liquid and vapour were in equilibrium. This model gave the location, starting time and amount of quenching required to prevent excess heating of the bed.

Panchenkov et al. (1977) modeled an industrial reactor which produced low pour point diesel fuel from gas oil by hydrocracking and isomerisation over a zeolite catalyst. A model for CANMET process based on a kinetic scheme was developed by Patmore and Pruden (1980). The experimental data closely agreed with the simulated result in the range 570-670 K and 10.44 - 17.34 MPa. Panaitescu and Dumitrescu (1982, 1983) suggested a model for hydrocracking of petroleum fractions. Using this model they obtained optimal conditions for steady state operating of a hydrocracking reactor. Due to the change in catalyst activity, the model constants have to re-evaluated from time to time. A model for hydrocracking of vacuum gas oil was developed by Laux (1983) which was based on product distribution vs boiling point index and structure index determined by the type of hydrocarbon product. The rate of hydrocracking could be determined from the change in these indices and the product distribution. Model developed by Mikshina et al. (1984) for hydrocracking of gasoline in a fixed catalyst bed consists of 33 equations including heat and material balances. The model was tested against pilot plant results.

2.2 HYDROTREATING

Crude petroleum, as well as petroleum fractions, contain

sulfur in the form of sulfides, disulfides, mercaptans and thiophenes which are undesirable since they are potential poisons for various catalysts used in further processing of petroleum fractions (Satterfield,1980). For example, reforming catalysts are very sensitive to sulfur and hence the sulfur content of the feed to the reformer should be made as low as possible. In case of very sensitive catalysts it may be necessary to lower the sulfur content to 1 ppm or less. Other problems associated with sulfur containing compounds present in petroleum fractions are the corrosion of process equipment and pollution of environment. Although sulfur is the major impurity, there are nitrogen compounds, oxygen compounds, hydrocarbon complexes containing metals and gum forming compounds which are usually undesirable and need to be removed.

The sulfur content of any crude largely depends on its origin (Gary and Handwerk, 1975; Satterfield, 1980) and may vary from 0.2 to 4.0 wt%. North African and Indonesian crudes are low in sulfur content ($\sim$ 0.2 wt%) whereas Venezuelan and Kuwait crudes have high sulfur content ($\sim$ 4 wt. %). Feedstocks used for hydrodesulfurisation (HDS) range from light naphthas (b.p.: C_4 - 350 K) to fuel oils (b.p.> 620 K). During HDS, hydrogen reacts with the sulfur bearing compounds, in the presence of a catalyst, to form hydrogen sulfide. This hydrogen sulfide can then be converted into elemental sulfur in a Claus type of process. Generally, hydrodenitrogenation (HDN), hydrodemetallation (HDM) and hydrodeoxygenation (HDO) take place simultaneously with HDS (Hohnholt amd Fausto, 1985). Based on the tonnage of treated products, HDS is even a more important process than catalytic cracking. About 25 to 30% of total liquid hydrocarbons extracted

annually are hydrodesulfurised (Delmon, 1981).

HDS process was initially stimulated by the availability of hydrogen from catalytic reformers. Later, when the demand for hydrogen increased, it was generated specifically for these purposes. The side reactions like HDN and hydrogenation of diolefins which take place simultaneously with HDS, improve the stability of the products, reduce gum formation besides reducing the rate of coke formation. Some of the multi-ring aromatics are broken down to single ring aromatics which are desired products for gasoline. By careful control of temperature and pressure, one can reduce hydrogenation of mono-olefins.

Since hydrogen is expensive to manufacture, it is necessary to operate all hydrotreating processes under optimum conditions which may depend upon the particular type of feedstock. Several review articles have appeared on HDS (Motegi, 1978; Laughout et al., 1980b; Asoaka and Nakamura, 1982; De la Cal and Asua, 1984) but most of these are restricted to specific aspects of the process.

2.2.1 Processes:

Hydrotreating is generally carried out by contacting hydrogen and petroleum fraction in gaseous or liquid phase with a solid catalyst in fixed or fluidised bed reactors. The basic equipment for hydrotreating is essentially the same regardless of the feed being processed. With proper conditions, any crude can be hydrotreated. A simple flow diagram for a hydrotreating process is given in Figure 2.2. It consists of a furnace where the hydrocarbon feed together with the make-up hydrogen is heated to the reaction temperature and sent to the multi-bed reactor. The
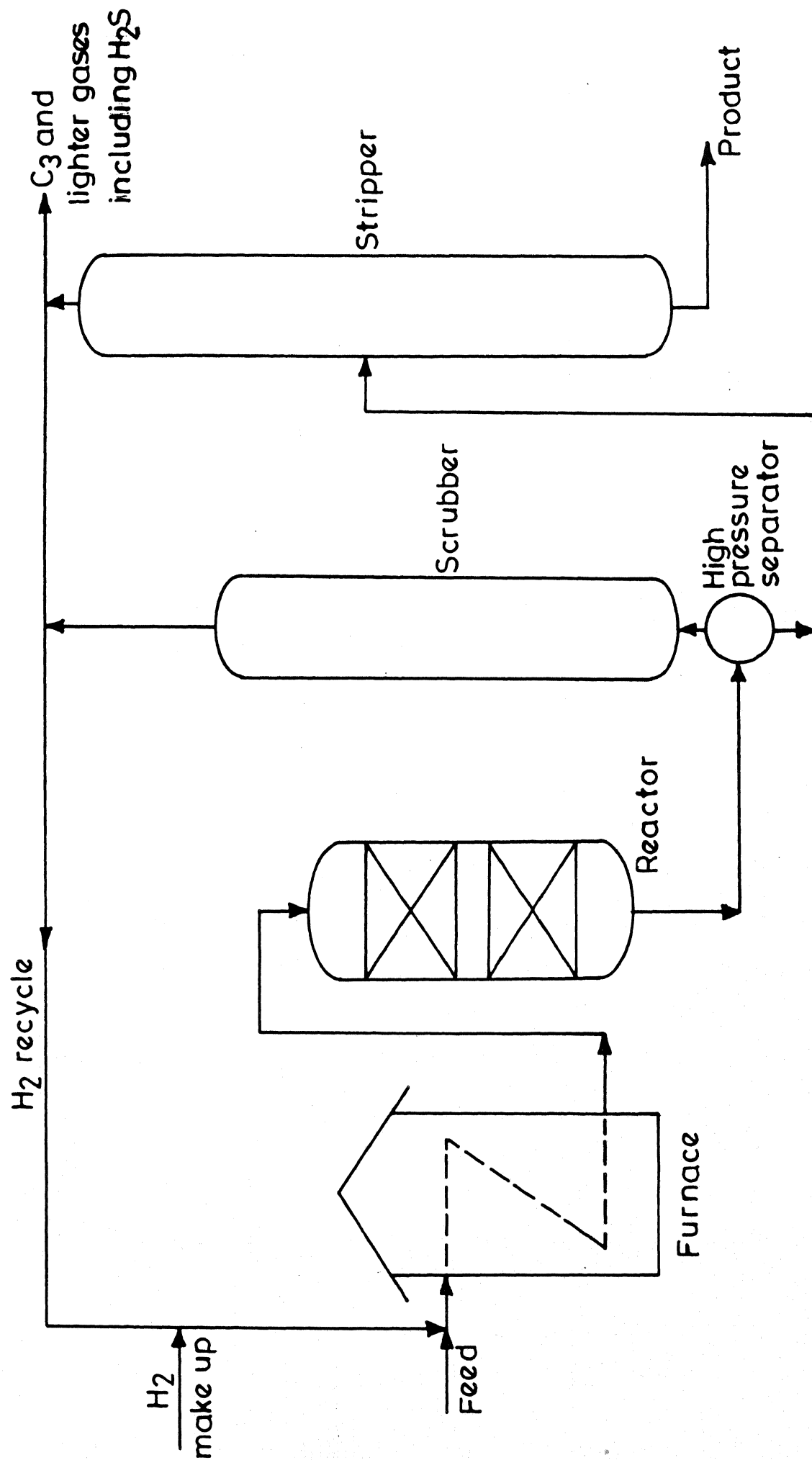
Fig. 2.2- A schematic diagram of a hydrotreating process.

effluent from the reactor is sent to a high pressure separator after which the gas is scrubbed and recycled. The liquid product is sent to a stripper where dissolved gases and unstabilised light distillates are separated from the desulfurised product. The oil flows in a single pass at a space velocity of 0.5 to 25 x 10^{-4} s^{-1} (volume per second of liquid oil at standard conditions per volume of packed bed reactor) depending on the temperature, pressure and degree of desulfurisation required. Reactor pressure is generally in the range from 2×10^{6} N/m^{2} to 1.5×10^{7} N/m^{2}. Operating temperature range is 575 - 700 K. Coke, which reduces the activity of the catalyst can be burnt off and the catalyst reused for many years (Schuit and Gates, 1973). In some processes, part of the hydrogen is used to provide cold shot cooling. Some other processes, particularly the ones using heavy fractions as feed, utilise two reactors in series with different catalysts and operating conditions to achieve desired removal of impurities. Additionally, a guard reactor is generally included when feeds are processed to remove metal impurities which might otherwise plug the reactor. Reviews on hydrotreating processes are given by Laughout et al.(1980a, 1980b) and McCulloch (1983). A number of processes have been licensed and further details are available in Petroleum Refinery Handbook (1986).

In addition to the commercial processes, several other studies have been carried out in the field of hydrotreating. HDS of straight run gasoline has been carried out by Mirzaev et al. (1976) over Ni-Mo catalyst at 640 -650 K, 1 to 4 MPa and liquid space velocity 3.0 - 7.0 h^{-1}. Sanchez (1978) has described a method in which hydrogen present in Mexican petroleum is used for removal of sulfur compounds from naphtha. The process is carried

out over a Co-Mo/γ-Al$_2$O$_3$ catalyst at 2.8 - 10.0 MPa and 570-690 K.

In the Tokoshi MDS direct HDS process for residual oils, the fresh catalyst is fed from the top of the reactors and the spent catalyst removed from the bottom. At the bottom, the spent catalyst comes in contact with the incoming oil and removes catalyst poisons before these reach the active catalyst (Suzuki et al., 1977). Another process of desulfurisation is to treat atmospheric residual oil with a CO-H$_2$O mixture. Takemura et al. (1981) have treated an atmospheric residual oil by this process over Co-Mo/Al$_2$O$_3$ catalyst using a batch autoclave at 623-673 K. Water-gas shift and desulfurisation reactions take place concurrently but the excess H$_2$O and CO$_2$ produced by the water-gas shift reaction inhibit the desulfurisation reaction.

Vail et al. (1980) carried out HDS of petroleum residue which was previously demetallised in a three phase fluidised bed reactor. The products obtained were C$_1$-C$_4$, gasoline, diesel oil, fraction for catalytic cracking and residue for coking. Gimaev et al. (1981) have carried out HDS of heavy gas oils with light aromatic in stationary bed of a Co-Mo/Al$_2$O$_3$ catalyst. The product contained less than 0.5% sulfur when the process was carried out at 673 K, 5 MPa and 1.0 h^{-1} space velocity.

Hydrodemetallation of heavy residual oil was conducted by van Dongen et al.(1980) in a trickle-flow reactor with liquid recycle at a laboratory-scale level. For heavy oil containing asphaltenes, a new process has been developed known as the Asphaltenic Bottom Cracking which uses a proprietary catalyst.

2.2.2 Chemistry

HDS, HDO, HDN, HDM as well as olefin, diolefin and

aromatics saturation are the major reactions taking place during hydrotreating.

Sulfur is generally present in the form of thiols (mercaptans), sulfides, disulfides, thiophene and thiophene derivatives. The sulfur compounds react with hydrogen to form hydrogen sulfide and hydrocarbons (Satterfield, 1980; McAfee, 1960). The various representative reactions are given below :

i)   RSH   + H_2 $\longrightarrow$ RH + H_2S
     (mercaptan)

ii) RSSR'   + H_2 $\longrightarrow$ RH + R'H + H_2S
     (disulfide)

iii) RSR'   + $2H_2$ $\longrightarrow$ RH + R'H + H_2S
     (sulfide)

iv)   + $3H_2$ $\longrightarrow$ H_2S + C_4H_8
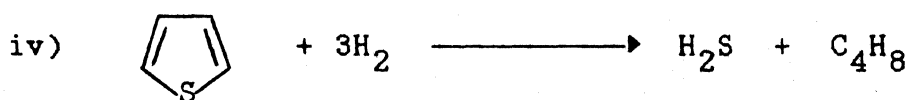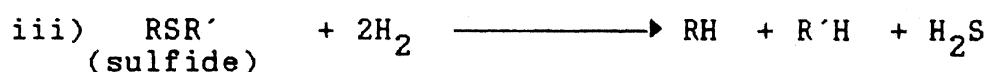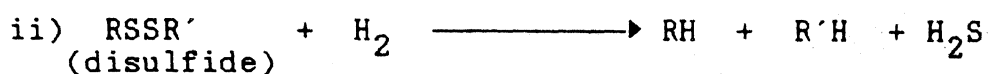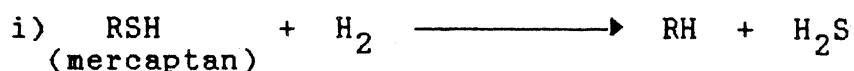
     (thiophene)

where R and R' are various hydrocarbon groups. Small amounts of butadiene formed during thiophene hydrogenation are hydrogenated to butene immediately. Thiophene is formed in small amounts in the absence of nitrogen and is completely absent in the presence of nitrogen. Reactivities of various sulfur compounds decrease in the following order :

RSH > RSSR' > RSR' > thiophenes

Reactivity depends on the molecular size and also upon whether R is an aliphatic or aromatic group. The reactivity of thiophene derivatives decreases as follows :

Thiophene > Benzothiophene > Methyl-substituted benzothiophene

In case of benzothiophene, the thiophene ring is hydrogenated to the thiophene derivatives before the sulfur is removed, as follows :

v) [benzothiophene structure] + H$_2$ $\longrightarrow$ [dihydrobenzothiophene structure] $\xrightarrow{2H_2}$ [ethylbenzene structure] CH$_2$CH$_3$ + H$_2$S
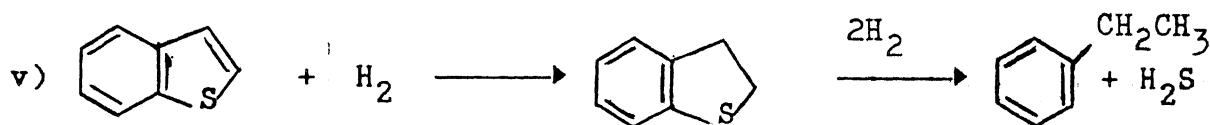
(benzothiophene)

Dibenzothiophene reacts to form mainly biphenyl and small amounts of phenyl cyclohexane.

vi) 2 [dibenzothiophene structure] +3H$_2$ $\longrightarrow$ [biphenyl structure] + [phenyl cyclohexane structure] +2H$_2$S

(dibenzothiophene)   (biphenyl)   (phenyl cyclo-
                                            hexane)
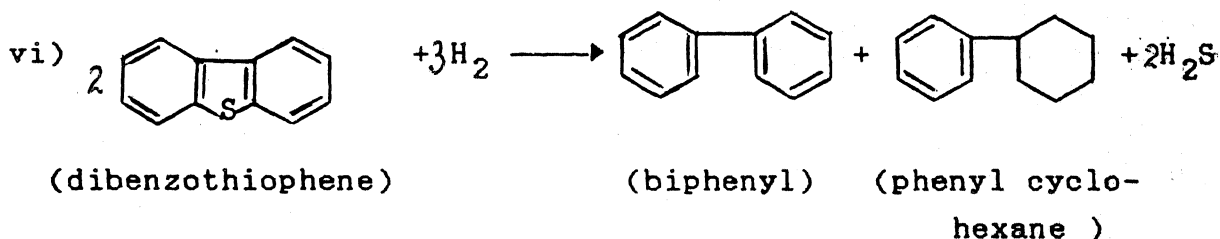
Biphenyl may be further hydrogenated to phenyl cyclohexane.

Almost all HDS reactions are irreversible. Thiophene has been used as the model reactant in research works since it is the most easily obtained compound. Amberg and coworkers (Owens and Amberg, 1961; Desikan and Amberg, 1963) have shown that hydrogen sulfide inhibits the reaction of thiophene and hydrogenation of butenes. In contrast to benzothiophenes, hydrogenated sulfur compounds are not intermediates in HDS of the more reactive thiophene (Givens and Venito, 1970; Schuits and Gates, 1973). Kilanowski et al. (1978) carried out HDS reactions of pure sulfur containing compounds at atmospheric pressure over sulfided CoO-MoO$_3$/γ-Al$_2$O$_3$ catalyst in a pulse microreactor and concluded that aromatic compounds react with hydrogen by simple sulfur

extrusion. Dibenzothiophene gave H_2S and biphenyl in the absence of side products. The reactivities of thiophenes, dibenzothiophenes and benzothiophenes were almost the same. Other studies on the reaction mechanism during HDS of thiophenic compounds include those by Houalla et al. (1978), Kwart et al. (1980) and Houlla et al. (1980).

Other reactions generally taking place during hydrotreating are deoxygenation, denitrogenation and saturation of olefins and aromatics. Oxygen containing compounds such as phenol and naphthenic acids are easily hydrogenated to form hydrocarbons and water. Nitrogen compounds present as impurities are in the form of pyridines, quinolines, isoquinolines, pyrroles, indoles and carbazoles. Ammonia is liberated during the hydrogenation of these compounds. These reactions take place less readily than those for oxygen and sulfur compounds. At normal hydrotreating pressures and temperatures, olefin hydrogenation is favoured. Above 570 K and in the presence of metallic catalysts, olefins may also undergo secondary cracking reactions. Aliphatic olefins and unsaturated ring compounds are more easily hydrogenated than aromatics. The chemistry of these oxygen, nitrogen, olefins and aromatic compounds are given by Horne and McAffe (1960) and Gary and Handwerk (1975).

2.2.4 Catalysts

The most commonly used catalyst for HDS is a mixture of Co and Mo oxides on a γ-alumina support (Beuther et al., 1959; Ashley and Mitchell, 1969; Furimsky, 1979) which is sulfided before use (Schuit and Gates, 1973). Topsoe et al. (1986) have reviewed the recent research carried out on HDS catalyst. Methods

of sulfiding are given by Patterson et al. (1976), Okamoto et al. (1979), Zingg et al. (1980), Schrader and Cheng (1983,1984) and McCarty and Schrader (1984). The effect of sulfidation on HDS and HDM has been studied by Gajardo et al. (1982) under industrial process conditions. Sulfidation enhances both HDS and HDM activity. The initial deactivation of sulfided catalyst is due to adjustment of degree of sulfiding of the catalyst surface rather than catalyst poisoning. The structure of sulfided catalyst is different from that of oxide precursors. These form a layered structure in which layer of sulfur atoms alternate with layers of metal atoms. The active sites are formed at the edges by the intercalation of Ni (or Co) into the MoS_2-WS_2 structure (Topsoe and Clausen, 1984). The effect of the pore size on the catalyst activity was studied by Plumail et al. (1983). For HDS, average pore diameter of 100 $\overset{o}{A}$ was found best and for HDM, 150-200 $\overset{o}{A}$. Sambi et al.(1982) have been able to remove 92% S and 72% N using a catalyst containing 3% CoO and 15% MoO_3 on an alumina support (Harshaw Co.) for hydrotreatment of a heavy gas oil. It has been reported that cobalt-molybdenum-alumina catalyst is very effective for the HDN of pyridine (Gupta et al., 1978). Ramirez De Agudelo (1984) have examined the effect of metal sulfides on hydrotreatment using silica and alumina supports. Both metal content and support affected the catalyst activity.

$Ni-Mo/Al_2O_3$ catalysts are used where hydrodenitrogenation and hydrogenation reactions are also important (Sambi et al., 1984). A recent review on hydrodenitrogenation has been given by Ho (1988). The effect of phosphorus on the activity and selectivity of $Ni-Mo/Al_2O_3$ has been studied by Fitz and Rase (1983). They found that the optimum

catalyst composition for HDS alone was a low-metals formulation with a medium phosphorus content whereas for nitrogen containing feeds high metals/high phosphorus catalyst was more suitable. Other studies on catalysts used for thiophene HDS has been reported by La Vopa and Satterfield (1988) and Yulin et al. (1988). Galiasso et al. (1985) used Ni-Mo/Al_2O_3, Co-Mo/Al_2O_3 and W-Ni/Al_2O_3 for their study on hydrotreatment of cracked gas oil. At low pressures, all catalysts showed the same activity but at high pressures, Ni-Mo catalyst improved colour, stability and octane number of high aromatic content feed. Iannibello et al. (1985) used Mo (VI) and W (VI) on bauxite catalysts for HDS of reduced crude from Adriatic Sea origin. Co and Ni were added as promoters. Caceres et al. (1986) studied the effect of promoters on HDS catalyst activity.

The nature of the support also has an effect on the activity of the catalyst. Iannibello et al. (1979) and Vecchi et al. (1982) have used bauxite supports instead of Al_2O_3 without significant reduction in the activity of the catalyst. De Beer et al. (1984) compared the activity of Co-Mo, Fe, and Mo catalysts prepared on Al_2O_3 or carbon supports for thiophene HDS. It was seen that HDS activity of Co-Mo and Fe catalysts increased in the order γ-Al_2O_3 < C-black composite < active carbon.

Zeolites have also been used in catalytic HDS process. X and Y zeolites were modified by ion-exchange or impregnation with Mo and Ni and compared with commercial Co-Mo catalysts in the HDS of vacuum distillates. The X zeolites had better HDS activity than Y zeolites and the activity was comparable with that of commercial catalysts (Mazur et al., 1980).

A catalyst with high resistance to coke deposition was

developed by Kiezel and Rutkowski (1980) by first coating the support with finely distributed carbon, then activating with steam and finally depositing the metals. Such a catalyst can be used for HDS of high molecular weight fractions. Bebar and Weisser (1983) have shown that a liquid film formed on the catalyst surface during HDS of heavy petroleum fractions in trickle bed reactors has an inhibiting effect on the reaction.

Nomura et al. (1980) studied the factors affecting the catalyst life. They used $CoO-MoO_3-SiO_2-Al_2O_3$ catalyst for HDS of residual petroleum oils in a fixed bed microreactor. The catalyst life depended on the physical properties of the catalyst as well as the feed oil and the operating conditions. Catalyst poisoning takes place due to deposition of metals and coke which plug the pores. Nomura et al. (1981) studied various causes of catalyst poisoning of atmospheric residual oil in microreactors. They found that vanadium was precipitated at the inlet and coke at the outlet of the catalyst bed and nickel was precipitated throughout the bed. When Ni was used as a promoter in a Ni-Mo catalyst, the extent of deactivation of fresh catalyst was reduced when exposed to a mixture of hydrogen and thiophene at atmospheric pressure. A series of experiments were carried out by Laine et al. (1985) on alumina supported catalysts of various Ni and Mo concentrations and it was found that Ni is involved in the initial transformation of molybdate catalysts. The role of Co and Ni in modified $Co(Ni)Mo-Al_2O_3$ catalyst for the HDS reaction was studied by Morales and Ramierz de Agudelo (1986).

A recent survey (Aalund, 1984) gives a comprehensive list of catalysts, which are manufactured by various companies. The given details include the nature of the active ingredient,

support and recommended applications.

2.2.4 Kinetics

Not much information is available on the kinetics of HDS of petroleum fractions. Most of the published studies have concentrated on thiophene or its derivative as a model compound (Kilanowski and Gates, 1980; Broderick and Gates, 1981; van Parijs and Froment, 1986; van Parijs et al., 1986).Vrinat (1983) and Ho (1988) have reviewed the kinetics of HDS and HDN processes respectively. Frye and Mosby (1967) reported that lower molecular weight compounds are more readily desulfurised as compared to high molecular weight compounds during the HDS of light catalytic cycle oil. These reactions were found to be first order in the concentration of the sulfur compounds for hydrogen pressure less than 2.8 MPa. These workers also reported that H_2S and aromatic hydrocarbons inhibit the rate of HDS. Satterfield and Roberts (1968) determined the kinetics of thiophene HDS in the absence of mass transfer influence on a commercial cobalt molybdate catalyst at a reaction temperature between 508 and 538 K and pressure in slight excess of the atmospheric. The data for rate of thiophene disappearance (hydrogenolysis) and that of butane formation (butene hydrogenation) were correlated with Langmuir-Hinshelwood rate equation.

Schuit and Gates (1973) found hydrogenolysis of each sulfur compound to be first order with respect to the partial pressure of that compound. The rate increased as the square root of the total pressure. The empirical relation given by them considering intraparticle mass transfer influence at pressures higher than atmospheric.

In addition to H_2S, nitrogen compounds can also inhibit HDS. Gutberlet and Bertolacini (1983) found that for conditions where hydrodenitrogenation was negligible, inhibition of HDS depended on the type and structure of the nitrogen compound involved. The inhibition effect could be accounted for by including an adsorption term for the nitrogen compound in the Langmuir-Hinshelwood model.

Ozaki et al. (1975) carried out HDS of residual oil in a commercial reactor. During five years of its operation, the order of reaction decreased from greater than 2 to 1.5 with a rise in reaction temperature. They developed expressions for evaluating catalyst life based on these kinetic studies and temperature gradient in the reactor. Yitzhaki and Aharoni (1977) studied the kinetics of HDS of fractions with boiling ranges of 20 K and mid-boiling points between 520-620 K. The reactions were considered to be first order. It was seen that rate constants for individual sulfur compounds of high molecular weight primarily depended on the molecular weight and not on the structure. Based on this, the fractions were lumped into homogeneous groups according to the boiling point. The feeds were gas oil and a mixture of gas oil and gasoline with different sizes of catalyst particles. The intrinsic kinetics of hydrogenolysis of thiophene on a $NiO-MoO_3-Al_2O_3$ catalyst was studied by Chakraborty and Kar (1978) in a differential reactor at a total pressure of 1 atm and temperature in the range of 510-563 K. Retardation of the reaction by H_2S was significant.

Nomura et al. (1979) used microreactors packed with $CoO-MoO- SiO_2-Al_2O_3$ catalyst for the HDS of petroleum residual oils. About 90% sulfur was removed and a second order reaction

observed with apparent activation energy of 105-125 MJ/kmol for atmospheric residues. The reaction rate constant increased linearly with increasing reaction pressure in the range 5-20 MPa. The reaction rate was negligibly affected by the hydrogen-oil volume ratio and the feed oil velocity. The rate of HDS was inversely proportional to the asphaltene content in the feed oil. Botnikov et al. (1980) carried out HDS of petroleum residues over stationary bed of Co-Mo-Al_2O_3 catalyst and found the reaction to be second order. Scamangas et al. (1981) reported that the rate of catalytic hydrodesulfurisation of an atmospheric distillation residue in a trickle-bed reactor was second order with respect to total sulfur and first order with respect to hydrogen pressure. The activation energy was computed to be 123 MJ/kmol. The validity of the formal power-law kinetic models for description of HDS reactions with experimental data obtained from laboratory and pilot plant reactors were tested by Schoengut et al. (1982). Optimal conditions for production of low sulfur fuel oil were evaluated.

Kinetics of HDS, HDN and hydrogenation of polynuclear aromatics were studied over five types of catalysts, $CoO/MoO_3/Al_2O_3/SiO_2$, $NiO/CoO/MoO_3/Al_2O_3$, $NiO/MoO_3/Al_2O_3$, $NiO/WO_3/Al_2O_3/SiO_2/TiO_2$ and MoO_3/Al_2O_3 by Chu and Wang (1982). The heterocyclic molecules and hydrogen molecules were assumed to be adsorbed on different types of catalyst sites. Considering the rate determining step as the surface reaction between adsorbed heterocyclic molecules with adsorbed hydrogen molecules, the rate equation was derived. The kinetics of hydrogenation of biphenyl on a sulfided $CoO-MoO_3/\gamma-Al_2O_3$ was studied by Sapre and Gates (1982) in the temperature range 573-648 K and pressure from 7 to 20 MPa

and several Langmuir-Hinshelwood type of kinetic models were proposed.

Pazos et al. (1983) studied the effect of catalyst properties and operating conditions on hydrotreatment of heavy oils having high metal content. They developed vanadium profiles along the reactor length under certain conditions based on which they developed a kinetic model which considered demetallization to be a complex reaction that occurs through a series of consecutive and parallel reactions.

Workers at Japan Petroleum Institute (1984) have carried out HDS of vacuum residual oils to determine the relationship between reaction rate and properties of the feed. The reaction rate was found to be well correlated with the Conradson carbon residue. Papayannakos and Marangozis (1984) studied the kinetics of catalytic HDS of an atmospheric distillation residue in a batch-recycle trickle-bed reactor with a commercial catalyst. Catalyst effectiveness, effective pore diffusivity and the activation energy. were determined quantitatively. Later, Papayannakos (1986) studied the effect of asphaltene content on the kinetics of HDS of an atmospheric distillation residue. The intraparticle diffusional effect on HDS reactions of a residue has been studied by Philippopoulos and Papayannakos (1988).

Sanford and Yui (1984) studied the kinetics of hydrotreating three synthetic distillate on pilot scale using Ni-Mo catalysts. Correlations were developed to predict the yield and some product properties. Mohammed (1984) subjected SAE-30 oil distillate (medium lubricating oil) to HDS on different types of Ni-Mo catalysts in the temperature range 553-636 K. The activation energy, enthalpy and entropy changes were calculated and it was

seen that the catalyst particle size significantly affected the rate of reaction. Stefan et al. (1985) studied the kinetics of HDS of gas oil over sulfided Co-Mo catalyst in the temperature range 553-633 K and pressure 2 to 6 MPa. They were able to express the kinetics by power rate law, with overall reaction order being one in the presence of H_2S and 3 when H_2S was removed by chemisorption on ZnO.

Satterfield and Cocchetto (1981) studied the kinetics of vapour-phase catalytic HDN of quinoline in a continuous flow microreactor on a presulfided $NiMo/Al_2O_3$ catalyst. The reaction rate was described by Langmuir-Hinshelwood type of expression. Under industrial conditions, the major product of HDN of quinoline was propylcyclohexane with propylcyclohexene as a significant intermediate. Presence of H_2S slightly inhibited the hydrogenation-dehydrogenation reactions but accelerated the overall HDN of quinoline in both vapor and liquid phases (Satterfield and Gultekin, 1981; Yang and Satterfield, 1984). The presence of water increased the rate of HDN of quinoline (Satterfield et al., 1985). Kinetic study on hydrodemetallation of porphyrin was made by Hung and Wei (1980a, 1980b).

2.2.5 Mass Transfer Effects

The various mass transfer effects during HDS may include interparticle mass transfer, intrapellet pore diffusion and the effect of internal and external catalyst wetting on the activity. A number of authors (Adlington and Thomson, 1965; Cecil et al., 1968) have conducted experiments on trickle bed reactors at constant space velocity and varying mass velocities. Mass transfer through the liquid film does not seem to offer significant

resistance under typical HDS conditions. Furthermore, the diffusion of hydrogen is much faster compared to the diffusion of the oil molecules. Based on a series of pilot experiments on heavy gas oil over a commercial $Co/Mo/Al_2O_3$ catalyst, van Deemter (1965) concluded that only catalyst particles with diameter well below 1 mm would show no diffusional resistance and that the diffusion coefficient of the sulfur compound is slightly lower than that for free liquid diffusion at 5 MPa and 648 K.

Fott and Schneider (1984) considered the effect of mass transport on the selectivity during thiophene HDS. They developed an isothermal model of a porous catalyst with a complex reaction and multicomponent diffusion in the transition region which was tested experimentally. The transport parameters and kinetic parameters needed for modeling were obtained experimentally. In case of HDS of a feedstock which contained small amounts of organo-sulfur compounds, the key reactant was a liquid phase component in low concentration. In such a case, the mass transfer from the film to the catalyst may become the rate-limiting step instead of transfer of dissolved gas through the film (Satterfield, 1975).

Schuit and Gates (1973) reported that external phase mass transfer does not influence the rate of HDS in well designed pilot-scale reactors and the external phase resistance in case of commercial reactors can be neglected since the mass velocities are quite high. In addition, they suggested that the effectiveness factors in HDS could be generalised to be slightly less than one for most feeds and catalysts. The effectiveness factors can change during catalyst aging.

The concept of liquid-solid contacting effectiveness has

been widely discussed in the literature (Satterfield, 1975; Gianetto et al., 1978). The main characteristic of a trickle-bed reactor is that the catalyst pellets are not completely wetted. Because of very poor liquid distribution and/or very rapid and highly exothermic reaction, the external surface of the catalyst may be partially wetted and a dry internal zone may develop. Limited research has been carried out on the effectiveness factor of a partially wetted pellet (Martinez et al., 1981).

When the liquid reactant is volatile and reaction can take place in the dry zone, then the reaction in the dry zone dominates the overall reaction (Satterfield and Ozel, 1973; Sedricks and Kenney, 1973). Martinez et al. (1981) analysed the effect of both internal and external wetting when the limiting reactant is in the gas phase and reaction takes place in the dry zone. It was assumed that the liquid phase reactant is sufficiently volatile so that the rate of reaction can be considered to be pseudo-first order with respect to the gas phase reactant. Mills and Dudukovic (1979) formulated a model for the case where the reactant is in the liquid phase and accounted for the effect of both fractional pore filling and partial external wetting on the effectiveness factor of a catalyst slab. Application of this model to trickle-bed reactor was outlined.

For hydrotreating of heavy residual oil, Iannibello et al. (1985) proposed models which incorporated the influence of hydrodynamics on the catalyst utilisation. These models generally assume plug flow and first order kinetics.

Baker (1978) also reported that a maximum catalyst utilisation was obtained when the catalyst were completely wetted. Iannibello et al (1983) have concluded that total pore filling may

be considered even at low liquid flow rate when the temperature is high. Ramachandran and Smith (1979) developed expressions for the overall effectiveness factor when the limiting reactant is either in the liquid phase or in the gas phase.

Sakornwimon and Sylvester (1982) developed an approximate explicit expression by using finite difference method for determination of effectiveness factor for spherical catalyst particles for three case; (i) liquid phase reaction with complete internal wetting (ii) vapour phase reaction with internal wetting and (iii) vapour phase reaction with incomplete internal wetting. The deviations from the corresponding numerical results and effect of various parameters on the performance of trickle-bed reactor for each case has been discussed.

Satterfield and Ozel (1973), Sedricks and Kenney (1973) and Herskowitz et al. (1979) concluded that the wetting efficiency is less than unity at very high liquid rates. The global rate was affected quite significantly by the external and intraparticle mass transfer when the catalyst was liquid full. In liquid full operation, the global rate decreased with decreasing liquid rate. Herskowitz (1981a) developed expressions for calculating the effectiveness factor when the surface concentration was non-uniform as a function of wetting efficiency, Biot number and Thiele modulus. Herskowitz (1981b) developed a computationally simple model which includes wetting efficiency as a parameter of the reactor performance for partially wetted catalysts and applied it to the analysis of oxidation of sulfur dioxide in water-filled porous and partially wetted activated carbon particles packed in a trickle-bed reactor. Dudukovic (1977) developed an expression for catalyst effectiveness factor for hydrodesulfurisers operating in

the regime free from external gas-liquid and liquid-solid mass transfer in terms of Thiele modulus, incomplete external wetting and fractional pore fill-up.

2.2.6 Reactor Modeling

To date, very few models have been reported in literature for hydrotreating reactors. Henry and Gilbert (1973) developed a model for a trickle-bed reactor which was tested against data obtained from a pilot plant HDS unit. The model showed that the catalyst utilisation increased with decreasing particle size as a result of increased hold-up. Eigenson and Maksinova (1976) presented a mathematical model for HDS of petroleum residues. Zhorov et al. (1977) modeled an adiabatic HDS reactor which can be used for the calculation of yield and sulfur content of the product.

Kodama et al. (1980) presented a model which considered active-site poisoning and pore plugging due to the interaction of demetallization and coking reactions. The catalyst activity is affected by reduction in surface area and effective diffusivity. The results obtained using this model were in good agreement with the bench scale data. The model is useful for predicting the reactor performance of both moving-bed and fixed-bed reactors.

BIBLIOGRAPHY

Abad-Zade, Kh.I.; Rustamov, M.I.; Akhmedov, V.M.; Mardanov, V.G. "Hydrocracking of Gasoline in the Presence of a Nickel-Aluminosilicate Catalyst Prepared from Organometallic Compounds" Azerb. Nefti. Khoz., 11, 48-50, 1984.

Aboul Gheit, A.K. "Hydrocracking of Vacuum Gas Oil (VGO) for Fuel Production. 1. Yields and Application" Erdoel, Erdgas, Kohle, 103(10), 441-444, 1987.

Adlington, D.; Thompson, E. "Desulfurisation in Fixed and Fluidised Bed Catalyst Systems" Third Eur. Symp. on Chem. React. Eng., Pergamon press, Oxford, 203-213, 1965.

Arayici, S.; Deymer, J. "The Role of Chloroform in Platforming" Chim. Acta Turc., 7, 213-223, 1979.

Archibald, R.C.; Greensfelder, B.S.; Holzman, G.; Rowe, D.H. "Catalytic Hydrocracking of Aliphatic Hydrocarbons" Ind. and Eng. Chem., 52, 745-750, 1960.

Asoaka, S.; Nakamura, M. "Treatment of Heavy Oil Hydrodesulfurisation and Removal of Metals" Petrotech (Tokyo), 5, 829-836, 1982.

Ashley, J.H., Mitchell, P.C.H. "Cobalt-Molybdenum-Alumina Hydrodesulfurisation Catalysts. Part II. Incorporation of Cobalt (II) and Molybdenum (VI) into γ-Alumina" J. Chem. Soc. A., 2730-2735, 1969.

Aalund, L.R., "Unique Survey Spotlights Complex Catalyst World" O & G J , 82(41), 55-88, 1984.

Baker, B. "Determination of the Extent of Catalyst Utilisation on a Trickle Flow Reactor" ACS Symp. Ser., 65 (Chem. React. Eng.), 425-435, 1978.

Baltanas, M.A.; Vansina, H.; Froment, G.F. "Hydroisomerisation and Hydrocracking. 5. Kinetic Analysis of Rate Data for n-Octane" Ind. Eng. Chem. Prod. Res. Dev., 22, 531-539, 1983.

Bebar, L.; Weisser, O. "Behavior of Trickle-Bed Reactors in Hydrodesulfurisation of Heavy Petroleum Fractions" Chem. Prum., 33, 169-175, 1983.

Bernardo, C.A.; Trinun, D.L. "Studies of the Negative Temperature Dependence Of the Rate of Carbon Formation on Nickel" Rev. Port. Quim., 19, 369-372, 1977.

Beuther, H.; Flenin, R.A.; Mc.Kinley, J.B. "For Better Hydrodesulfurisation Activity of Promoted Molybdenum Oxide-Alumina Catalysts" Ind. Eng. Chem., 51, 1349-1350, 1959.

Beuther, H.; Mansfield, R.F.; Stauffer, H.C. "Cost of Hydrogenating Lube Oils" Hy. Proc., 45(5), 149-152, 1966.

Billon, A.; Franck, J.P.; Peries, J.P. "Consider Hydrorefining for Lubes", Hy. Proc., 54(9), 139-144, 1975.

Botnikov, A.Y.; Rysakov, M.V.; Rogov, S.P.; Tychkin, U.S. "Macrokinetic Mechanisms of Hydrodesulfurisation of Residual Material" Sb. Nauchn. Tr.-Vses. Naucho-Issled. Inst. Pererab. Nefti, 38, 33-38, 1980.

Broderick, D.H.; Gates, B.C. "Hydrogenolysis and Hydrogenation of Dibenzothiophene Catalysed by Sulfided $CoO-MoO_3/\gamma-Al_2O_3$: The Reaction Kinetics" AIChE J., 27(4) 663-672, 1981.

Busch, R.A.; Kociscin, J.J.; Shroeder, H.F.; Shah, G.N. "Coke Heavy Stocks, Then Treat" Hy. Proc., 58(9), 136-142, 1979.

Bussel, M.E.; Gellman, A.J.; Somorjai, G.A. "Thiophene Hydrodesulfurisation over Transition Metal Surfaces : Structure Insensitive Over Molybdenum and Structure Sensitive Over Rhenium" J. Catal., 110(2), 423-426, 1988.

Caceres, C.; Fierro, J.L.G.; Lopez, A.A.; Severino, F.; Laine, J. "Relation Between HDS Activity and the State Of Promoters In Precursor Calcined Nickel-Cobalt-Molybdenum/Alumina Catalyst" J. Catal., 97, 219-227, 1986.

Cecil, R.R.; Mayer, F.X.; Cart, E.N. "Fuel Oil Hydrodesulfurisation Studies in Pilot Plant Reactors" paper presented at Am. Inst. Chem. Eng. Meeting, Los Angeles, 1968.

Chakraborty, P.; Kar, A.K. "Kinetics of Hydrolysis of Thiophene in Naphtha", Ind. Eng. Chem. Process Des. Dev., 17, 252-255. 1978.

Chen, N.Y.; Maziuk, J.; Schwartz, A.B.; Weisz, P.B. "Selectoforming - New Process to Improve Octane and Quality" O & G J, 66(47), 154-157, 1968.

Chesnokov, A.A.; Kogan, L.D.; Kozlova, N.M.; Chesnokova, N.Z., "Basic Hydrocarbon Conversions During Hydrorefining of Residual Raffinate", Khim. Technol. Topl. Masel, 4, 32-34, 1985.

Choudhary, N.; Saraf, D.N. "Hydrocracking :A Review" Ind Eng. Chem. Prod. Res. Dev., 14, 74-83, 1975.

Choudhary, N.; Saraf, D.N. "Hydrocracking of Assam Crude Residue for Middle Distillates Over LaX and NaX Catalysts" Ind. Eng. Chem. Prod. Res. Dev., 17, 196-202, 1978.

Chu, C.I.; Wang, I. "Kinetic Studies on Hydrotreating" Ind. Eng. Chem. Proc. Des. Dev, 21, 338-344, 1982.

Coates, R.; Myers, E.C.; Sue-A-Quan, T.A. "Desulfurization of Cat Cracked naphthas with Minimal Octane Loss" Natl. Pet. Refiners Assoc. (Tech. Pub), AM-78-52, 1978.

Coonradt, H.L.; Garwood, W.E. "Mechanism of Hydrocracking Reaction of Paraffins and Olefins" Ind. Eng. Chem. Proc. Des. Dev., 3, 38-45, 1964.

De Beer, V.H.J.; Derbyshire, F.J.; Groot, C.; Prins, R.; Scaroni,

A.W.; Solar, J.M. "Hydrodesulfurisation Activity and Coking Propensity of Carbon and Alumina Supported Catalysts" Fuel, **63**, 1095-1100, 1984.

De la Cal, J.C.; Asua, J.M. "Hydrodesulfurisation of Petroleum Fractions" Ing. Quim. (Madrid), **16**(186), 27-37, 1984.

Delmon, B. "Cobalt in Catalysts for Major Processes: Hydrodesulfurisation and Hydrotreating" Proc. Int. Conf. Cobalt-Metall. Uses, **2**, 285-294, 1981.

Demeester, J., Helion, R. "Wax Gets Two-Stage Hydrogenation" Hy. Proc., **47**(5), 177-179, 1968.

Desikan, P.S.; Amberg, C.H. "Catalytic HDS of Thiophene. IV. The Methyl Thiophenes" Can. J. Chem., **41**, 1866-1971, 1963.

Dudukovic, M.P. "Catalyst Effectiveness Factor and Contacting Efficiency in Trickle-Bed Reactors" AIChE J., **23**, 940-944, 1977.

Eccles, R.M.; Gray, A.M.; Livington, W.B. "New Resid Conversion Scheme Set for Louisiana Refinery" O & G J, **80**, 121-129, 1982.

Egan, C.J.; Langlois, G.E.; White, R.J. "Selective Hydrocracking of C_4 to C_{12}- Alkylcyclohexanes on Acidic Catalysts. Evidence for the Paring Reaction" J. Am. Chem. Soc., **84**, 1204-1219, 1962.

Eigenson, S.A.; Maksimova, N.E. "Mathematical Model of Heterogeneous - Catalytic Hydrodesulfurisation of Petroleum Residues", Mater. Resp. Nauchno-Tekh. Konf.Molodykh Uch. Pererab. Nefti Neftekhim, 3rd, **1**, 65-67, 1976.

Eleazer, A.E.; Heek, R. M.; Witt, M.P. "Hydroisomerisation of C_4S", Hy. Proc., **58**(5), 112-118, 1979.

El-Kady, F.Y.A. "Hydrocracking of Vacuum Distillate fractions Over Bifunctional Molybdenum-nickel/Silica-alumina Catalyst" Ind. J. Tech., **17**, 176-183, 1979.

El-Kady, F.Y.A.; Menoufy, M.F.; Hassan, H.A. "Effect of the

Reaction Temperature and Pressure on the Hydroisomerisation of n-Heptane" Ind. J. Tech., 21, 293-299, 1983a

El-Kady, F.Y.A.; Menoufy, M.F.; Hassan, H.A. "Reaction Mechanism and Order Rate of n-Heptane Isomerisation" Ind. J. Tech., 21, 300-305, 1983b.

Fitz, C.W.; Rase, H.F. "Effects of Phosphorous on Nickel-Molybdenum Hydrodesulfurisation / Hydrodenitrogenation Catalysts of Varying Metals Content" Ind. Eng. Chem. Prod. Res. Dev., 22, 40-44, 1983.

Flinn, R.A.; Larson, O.A.; Beuther, H., "The Mechanism of Catalytic Hydrocracking" Ind. Eng. Chem., 52, 153-156, 1960.

Fott, P.; Schneider, P. "Mass Transport and a Complex Reaction in Porous Catalyst Pellets: Thiophene Hydrodesulfurisation" Chem. Eng. Sc., 39(4), 643-650, 1984.

Franck, J.P.; Le Page, J.F., "Catalysts for the Hydrocracking of Heavy Gas Oils into Middle Distillates" Stud. Surf. Sci. Catal., 7 (Pt. B, New Horiz. Catal.), 792-803, 1980.

Friz, J.F.; Ternan, M.; Denis, J.M. "Upgrading by Hydrocracking : Selected Area of Research and Development Interest at CANMET", JCPT, 22, 29-34, 1983.

Frye, C.G.; Mosby, J. F. "Kinetics of Hydrodesulfurisation" Chem. Eng. Prog., 63(9), 66-70, 1967.

Furimsky, E. "Catalytic Removal of Sulfur, Nitrogen and Oxygen from Heavy Gas Oil" AIChE J., 25, 306-311, 1979.

Gajardo, P.; Pazor, J.M.; Salazar-Guillen, A. "Comments on the Hydrodesulfurisation, Hydrodemetallation and Hydrodenitrogenation Activities of Commercial Catalysts in the Hydrotreating of Heavy Crude Oil" Appl. Catal., 2(4-5), 303-313, 1982.

Galiasso, R.E.; Badras, C.; Garcia, W.J.; De Agudelo, M.M.R.;

Rodriguez, E., "Hydrotreatment of Cracked Light Gas Oils" Rev. Tec. INTEVEP, 5, 175-188, 1985.

Gary, J.H.; Handwerk, G.E. "Petroleum Refining: Technology and Economics" Marcel D,ekker, Inc., New York, 1975.

Gembicki, V.A.; Andermann, r.E.; Tajbl, D.G. "Mild Hydrocracking Fills Processing Gap" O & G J, 81(8), 116-128, 1983.

Gerdes, K.F.; Stangeland, B.E.; Chen, G.T.S.; Gumerman, R.J. "Simulation of Hydrocracking Reactor Systems" paper presented at the Annual Meeting of AIChE, 1977.

Ghosal, G.K. "Hydrocracking of Straight-Run Vacuum Gas Oil (350-500 °C) of North Rumaila (Iraq) Crude" Chem.Eng., 20(9), 83-85, 1985.

Gianetto, A.; Baldi, G.; Specchia, V.; Sicardi, S. "Hydrodynamics and Solid-Liquid Contacting Effectiveness in Trickle-Bed Reactors" AIChE J., 24, 1087-1104, 1978.

Gimaev, R.N.; Akhmetshina, M.N.; Vezirova, S.G.; Telyashev, G.G.; Potukhim, L.E. "Hydrodesulfurisation of Heavy Gas Oils from Destructive Processes" Neftepererab Neftekhim (Moscow), 10, 16-19, 1981.

Goldfarb, Y.Y.; Katsobashvili, Y.R.; Rozental, A.L."Study of Catalytic Hydrocracking of n-Decane, n-Undecane, N-Dodecane During Long Catalysis Periods" Kinet. Katal., 22, 668-674, 1981.

Grange, P. "Catalytic Hydrodesulfurisation" Cat. Rev.- Sci. Eng., 21(1), 135-181, 1980.

Grendele, G.V. "Kinetic Model for the Hydrocracking Reactions" Simp. Ieberoam. Catal., [Trab.], 7th, 469-478, 1980.

Gupta, R.K.; Mann, R.S.; Gupta, A.K., "Hydrodenitrogenation of Pyridine Over a Cobalt-Molybdenum-Alumina Oxide Catalyst", J. Appl. Chem. Biotechnol., 28(10), 641-648, 1978.

Gutberlet, L.C.; Bertolacini, R.J. "Inhibition of HDS by Nitrogen Compounds" Ind. Eng. Chem. Prod. Res. Dev., 22, 246-250, 1983.

Hargrove, J.D.; Elkes, G.J.; Richardson, A.H. "New Dewaxing Process Woven in Operations" O & G J, 77(3), 103-105, 1979.

Henry, H.C.; Gilbert, J.B. "Scale-up of Pilot Plant Data for Catalytic Hydroprocessing" Ind. Eng. Chem. Process Des Dev., 12, 328-333, 1973.

Herskowitz, M.; Carbonell, R.G.; Smith, J.M. "Effectiveness Factors and Mass Transfer in Trickle-Bed Reactors" AIChE J., 25, 272-281, 1979.

Herskowitz, M. "Wetting Efficiency in Trickle-Bed Reactor: The Overall Effectiveness Factor of Partially Wetted Catalyst Particles" Chem. Eng. Sci., 36, 1665-1671, 1981a.

Herskowitz, M. "Wetting Efficiency in Trickle-Bed Reactors: Its Effect on the Reactor Performance" Chem. Eng. J., 22, 167-175, 1981b.

Ho, T.C. "Hydrodenitrogenation Catalysis" Catal. Rev.-Sci. Eng., 30(1), 117-160, 1988.

Hohnholt, J.F.; Fausto, C.Y. "Upgrading Residual Oil by Fixed Bed Hydroprocessing" Chem. Eng. Prog., 81(6), 47-53, 1985.

Horne, W.A.; McAffe, J. "Hydrogenation of Petroleum and Its Fractions" in Ad. Pet. Chem., Vol III, Ed. McKetta, Jr., J.J., Interscience, New York, 1960.

Houalla, M.; Nag, N.K.; Sapre, A.V.; Broderick, D.H.; Gates, B.C. "Hydrodesulfurisation of Dibenzothiophene catalysed by sulfided $CoO-MoO_3/\gamma-Al_2O_3$: The Reaction Network" AIChE J., 24, 1015-1021, 1978.

Houlla, M.; Broderick, D.H.; Sapre, A.V.; Nag, N.K.; de Beer, V.H.J.; Gates, B.C.; Kwart,H. "Hydrodesulfurisation of Methyl

Substituted Dibenzothiophene Catalysed by Sulfided Co-Mo/γ-Al$_2$O$_3$"
J. Catal., 61(2), 573-527, 1980.

Hung, C.W.; Wei, J. "The Kinetics of Porphyrin Hydrodemetallation
1. Nickel Compounds" Ind. Eng. Chem. Process Des. Dev., 19,
250-257, 1980a.

Hung, C.W.; Wei, J. "The Kinetics of Porphyrin Hydrodemetallation.
2. Vanadyl Compounds" Ind. Eng. Chem. Process Des. Dev., 19,
257-263, 1980b.

Iannibello, A.; Marengo, S.;Girelli, A. "Refining of Heavy Crude
Oils: Hydrogen Treating on Bauxite Activated by Molybdenum Oxide"
Riv. Combust., 33(11-12), 373-383, 1979

Iannibello, A.; Marengo, S.; Guerci, A.; Baldi, G.; Sicardi, S.
"Performance of a Pilot Trickle-bed Reactor for Hydrotreating of
Petroleum Fraction : Dynamic Analysis" Ind. Eng. Chem. Process
Des. Dev., 22, 594-598, 1983.

Iannibello, A.; Marengo, S.; Burgio, G.; Baldi, G.; Sicardi, S.,
"Modeling of the Hydrotreating Reactions of a Heavy Residual Oil
in a Pilot Plant Trickle_Bed Reactor", Ind. Eng. Chem. Process
Des. Dev., 24, 531-537, 1985.

Idemitsu Kosans Chiba, Japan "First Lubricant-Oil Cracker has
Trouble-Free Record." O & G J, 70(24), 94-97, 1972.

Ireland, H.R.; Redini, C.; Raff, A.S.; Fava, L. "Distillate
Dewaxing in Operation" Hy. Proc., 119-122, 1979.

Jaeckh, C.; Dreyer, H.D.; Himmel, W.F.; Schlimper, H.U.; Spahl,
R.A. " Mild Hydrocracking: A New Route to More of Lighter
Distillates" Actas Simp. Iberoam. Catal., 9th, 2, 1226-1236, 1984.

Jaffe, S.B. "Hot Spot Simulation in Commercial Hydrogenation
Processes" Ind. Eng. Chem. Process Des. Dev., 15, 410-416, 1976.

Japan Petroleum Institute "Characterisation of Heavy Oils and its

Application. Part 8. Hydrodesulfurisation of Heavy Oils" Sekiya Gakkaishi, **27**(2), 164-169, 1984.

Katsobashvili, Y.R.; Teplyakova, G.A. "Production of Light Fuels by Hydrocracking of Bituminous High-Sulfur Petroleums" Khin. Tekhnol. Topl. Masel, **8**, 8, 1984.

Kelly, J.F.; Ternan, M. "Hydrocracking Athabasca Bitumen with Alkali Metal Promoted $CaO-MoO_3-Al_2O_3$ Catalysts" Can. J. Chem. Eng., **57**(6), 726-733, 1979.

Kiezel, L.; Rutkowski, M. "Catalysis for Hydrodesulfurisation of High-Molecular-Weight Fractions of Petroleum" Pol. Patent PL 108,972, 1980.

Kilanowski, D.R.; Teeuwen, H.; De Beer, V.H.J.; Gates, B.C.; Schuit, G.C.A.; Kwart, H. "Hydrodesulfurisation of Thiophene, Benzothiophene, Dibenzothiophene, and Related Compounds Catalysed by Sulfided Cobalt Oxide - Molybdenum Trioxide / γ-Alumina: Low-Pressure Reactivity Studies" J. Catal., **55**(2), 129-137, 1978.

Kilanowskii, D.R.; Gates, B.C. "Kinetics of Hydrodesulfurisation of Benzothiophene Catalysed by Sulfided $Co-Mo/Al_2O_3$" J. Catal. **62**, 70-78, 1980.

Koch, N.D.; Traylor, R.W. "Low-Fuel-Oil Refinery Makes Use of Hydrocracking Advances" O & G J, **79**(22), 102-105, 1981.

Kodama, S.; Nitta, H.; Takatsuka, T.; Yokoyama, T., "Simulation of Residua Hydrodesulfurisation Reaction Based on Catalyst Deactivation Model" Sekiyu Gakkaishi, **23**(5), 310-320, 1980.

Kondo, T.; Ojima, Y.; Ukegawa, K.; Sasaki, Y.; Matsumura, A.; Nakamura, E. "Hydrocracking of Residual Oil with Cobalt-Molybdenum-Aluminium Oxide Catalyst. Loss of Catalyst Activity and Properties of Product Oil" Kogai Shigen Kenkyusho Iho, **11**(4), 41-46, 1982.

Kondo, T.; Ojima, Y.; Ukegawa, K.; Sasaki, Y.; Matsumura, A.; Shimizu, Y.; Nakamura, E.; Sakabe, T., "Catalytic Hydrocracking of Heavy Oil" Kogai Shigen Kenkyusho Hokaku, 33, 1-70, 1984.

Kotowski, W.; Bebenek, S. "Innovations in Hydrocracking of Vacuum Distillates" Nafta (Katowice, Pol.), 37(6), 209-213, 1981.

Kotowski, W., "Hydrocracking of Atmospheric Distillation Residue with Iron-Nickel-Vanadium Catalyst" Nafta (Katowice, Pol.), 38(11-12), 232-236,1982.

Kotowski, W. "Two-Stage Hydrocracking of Fuel Oil with Coal" Chem. Tech. (Leipzig), 35(1), 22-23, 1983.

Kwart, H.; Schuit, G.C.A.; Gates, B.C. "Hydrodesulfurisation of Thiophenic Compounds: The Reaction Mechanism" J. Catal., 61, 128-134, 1980.

Laine, J.; Brito, J.; Gallardo, J.; Severino, F. "The Role of Nickel in the Initial Transformations of Hydrodesulfurisation Catalyst" J. Catal., 91, 64-68, 1985.

Langlois, G.E.; Sullivan, R.F. "Chemistry of Hydrocracking" Reprinted from Adm. Chem. Ser., No.9, 1970.

Laughout, W.C.Z.; Ouwerkerk, C.; Pronk, K.M.A., "New Process Hydrotreats Metal-rich Feedstocks" O & G J, 78(48), 120-126, 1980b.

Laughout, W.C.Z.; Ouwerkerk, C.; Pronk, K.M.A., "The Shell Residue Hydroprocesses" Proc. Symp. Catal. Reforming, Hydrotreating, Hydrocracking, 230-250, 1980a (Pub. 1981).

Laux, H., "Mathematical Model for the Hydrocracking of Crude Oil Vacuum Distillate" Chem. Tech. (Leipzig), 35(1), 8-11, 1983.

La Vopa, V.; Satterfield, C.N. "Poisoning of Thiophene Hydrodesulfurisation by Nitrogen Compounds" J. Catal., 110(2), 375-387, 1988.

Light, S.D.; Bertam, R.V.; Ward, J.W. "Hydrocrack Heavier Feeds" Hy. Proc., 60(5), 93-95, 1981.

Lumin, G.; Silva, A.E.; Denis, J.M. "The CANMET Hydrocracking Process- Upgrading of Cold Lake Heavy Oil" Chem. Can., 33(3), 17-21, 1981.

Marin, G.B.; Froment, G.F. "Reforming of C_6 Hydrocarbons on a Pt-Al_2O_3 Catalyst" Chem. Eng. Sci., 37(5), 759-773, 1982.

Martinez, O.H.; Barreto, G.F.; Lencoff, N.O. "Effectiveness Factor of a Catalyst Pellet in a Trickle-Bed Reactor. Limiting Reactant in the Gas Phase" Chem. Eng. Sci., 36, 901-907, 1981.

Mavity, V.T.; Ward, J.W.; Whitebread, K.E. "Unicracking for Petrolchemicals" Hy. Proc., 57(11), 157-160, 1978.

Maxwell, I.E. "Hydrocracking: Current Technology and Recent Developments" Ingenieursblad, 52(2), 53-58, 1983.

Mazur, K.; Wrzyszcz, J.; Ihnatowicz, M. "Hydrodesulfurising of Oil Fractions in the Presence of Catalysts Containing Zeolites" Nafta (Katowice, Pol.), 36(5), 165-169, 1980.

McCarty, K.F.; Schrader, G.L. "Hydrodesulfurisation by Reduced Molybdenum Sulfides: Activity and Selectivity of Chevrel Phase Catalyst" Ind. Eng. Chem. Prod. Res. Dev., 23, 519-524, 1984.

McCulloch, D.C., "Catalytic Hydrotreating in Petroleum Refining" Appl. Catal., 1, 69-121, 1983.

Miklena, V.S.; Hofman, N.; Martynenko, V.G.; German, V.D.; Flonya, V. "Analysis of Kinetic Models of the Hydrocracking of n- Alkanes" Materialy 3-i Vses. Konf. po Kinet. Geterogen. Katalitich. R-Tsii, Kalinin, 2, 302-309, 1980.

Mikshina, V.S.; Martynenko, V.G.; Taganov, I.N. "Study of the Hydrocracking of Gasolines via Models of Continuous Compositions" Khim. Technol (Kiev), 5, 8-9, 1984.

Mills, P.L.; Dudukovic, M.P. "A Dual-Series Solution for the Effectiveness Factor of Partially Wetted Catalysts in Trickle-Bed Reactors" Ind. Eng. Chem. Fundam., 18, 139-149, 1979.

Mirzaev, A.A.; Abdukadyrov, A.A.; Filippova, O.N.; Abidov, B. "Hydrodesulfurisation of Light Prtroleum Distillates over Zeolite-Containing Catalysts" Mater. Resp. Naucho-Tekh. Konf. Motodykh Uch. Pererab. Nefti Neftekhim, 3rd, 1, 26, 1976.

Mohammed, A.H.A.K., "Hydrodesulfurisation of Medium Lubricating Base Oils on Commercial Nickel-Molybdenum-Alumina Catalyst" J. Pet. Res., 3(2), 33-43, 1984.

Morales, A.; Ramirez de Agudelo, M.M. "Promoter Role of Octahedral Co (and Ni) in Modified Co (Ni) Mo-Al_2O_3 Catalysts for HDS Reactions" Appl. Catal., 23(1), 23-34, 1986.

Morita, M.; Hirosawa, K.; Sato, T.; Ouchi, K. "Supported Molten Zinc Chloride Catalysts. Part I. Comparison of Catalytic Activities for Hydrocracking" J. Jap. Pet. Inst., 23(1), 52-58, 1980.

Motegi, K. "Advances in Heavy Oil Desulfurisation Technology" Nenryo Kyokaishi, 57(10), 803-816, 1978.

Nakata, S.; Shiroto, Y.; Takahashi, H.; Takeuchi, C. "Characteristic Changes of Petroleum Residues by Thermal Treating and Catalytic Hydrotreating" Collect. Colleq. Semin. (Inst. Fr. Pet.), 40 (Caract Huiles Lourdes Residus Pet), 508-512, 1984.

Nasution, A.S. "Hydrocracking of Kuwait Vacuum Distillate and Lubricant Base Stock Production" Proc. Pac. Chem. Eng. Congr., 3rd, 2, 232-237, 1983.

Nasution, A.S. "Hydrocracking of Vacuum Distillate for Middle Distillate Production" Int. Semin. New Dev. Engine Oils, Ind. Oils, Fuels Addit., (Proc.), 5th, 1985.

Panchenkov, G.M.; Gorlov, S.G.; Belov, N.N.; Kolesnikov, I.M.; Zh. Fiz. Khim., 57(10), 2479-2486, 1983.

Papayannakos, N.; Marangozis, J. "Kinetics of Catalytic Hydrodesulfurisation of a Petroleum Residue in a Batch-Recycle Trickle-Bed Reactor" Chem. Eng. Sci., 39(6), 1051-1061, 1984.

Papayannakos, N. "Kinetics of Catalytic Hydrodesulfurisation of a Deasphalted Oil and of the Asphaltenic and Non-Asphaltenic Fractions of a Petroleum Residue" Appl. Catal., 24(1-2), 99-107 1986.

Patmore, D.J.; Pruden, B.B. "Thermal Hydrocracking of Athabasca Bitumen: Comparison of Computer Simulated Values of Feed and Product Vapourisation with CANMET Pilot Plant Data" CANMET Report 80-23E, Canada Centre for Mineral and Energy Technology, 21pp, 1980.

Patterson, T.A.; Carver, J.C.; Leyden, D.E.; Hercules, D.M., "A Surface Study of Cobalt-Molybdenum-Alumina Catalysts Using X-ray Photoelectron Spectroscopy" J. Phy. Chem., 80(15), 1700-1708, 1976.

Pazos, J.M.; Gonzalez, J.C.; Salazer-Guillen, A.J. "Effect of Catalyst Properties and Operating Conditions on Hydroprocessing High Metal Feeds" Ind. Eng. Chem. Process Des. Dev., 22, 653-659, 1983.

Phillippopoulos, C.; Papayannakos, N. "Intraparticle Diffusional Effects and Kinetics of Desulfurisation Reactions and Asphaltenes Cracking During Catalytic Hydrotreatment" Ind. Eng. Chem. Res., 27(3), 415-420, 1988.

Plumail, J.C.; Jacquin, Y.; Martino, G. "Effect of the Pore Size Distribution on the Activities of Alumina-Supported Co-Mo Catalysts in the Hydrotreatment of Boscan Crude" Prep. Am. Chem.

Soc., Div. Pet Chem., 28(3), 562-575, 1983.

Qader, S.A.; Hill, G.R. "Hydrocracking of Gas Oil" Ind. Eng. Chem. Process Des. Dev., 8(1), 98-105, 1969.

Rabinovich, G.B.; Borisevich, Y.P.; Levinter, M.E.; Rodionov, A.V. "Kinetics of the Conversion of n-Heptane on a Polymetallic Reforming Catalyst" Izv. Vyssh. Uchebn. Zaved., Khim. Khim Tekhnol., 26(6), 214-218, 1983.

Radchenko, E.D.; Gorshtein, A.B.; Shkol'nik, B.L.; Shtein, V.I. "Development of Hydrocracking of a Vacuum Distillate in Motor Fuel Production" Sb. Nauchn. Tr.-Vses., 44, Pb.2, 100-113, 1983.

Ramachandran, P.A.; Smith, J.M. "Effectiveness Factors in Trickle-bed Reactors" AIChE J., 25(3), 538-542, 1979.

Ramierz De Agudelo, M.M. "Role of Transition Metal Sulfides in Hydrotreatment. First Row Transition Metal Studies" Rev. Tec. INTEVEP, 4(1), 19-26, 1984.

Raseev, S.D.; El Kharashi, S. "Study on Hydrocracking of Gasoline (80-160 °C) Fraction IV. Mechanism" Rev. Chim., 29(12) 1140-1147, 1978.

"Refining Process Handbook" Hy. Proc., 65(9), 1986.

Reilly, J.W.; Sze, M.C.; Saranto, U.; Schmidt, U. "Aromatic Reduction Process is Commercialised" O & G J., 71(38), 66-68, 1973.

Sakabe, T,; Yagi, T. "Crack Resid with Spent HDS Catalyst" Hy. Proc., 58(12), 103-107, 1979.

Sakornwimon, W.; Sylvester, N.D. "Effectiveness Factors for Partially Wetted Catalysts in Trickle-Bed Reactors" Ind. Eng. Chem. Process Des. Dev., 21, 16-25, 1982.

Sambi, I.S.; Khulbe, K.C.; Mann, R.S. "Catalytic Hydrotreatment of Heavy Gas Oil" Ind. Eng. Chem. Prod. Res. Dev., 21, 575-580, 1982.

Sambl, I.S.; Khulbe, K.C.; Mann, R.S. "Catalytic Hydrotreatment of Hydrodesulfurisation Reactor Based on a Kinetic Model" Acta. Simp. Iberoam Catal.,9th, 2, 1295-1302, 1984.

Sanchez, M.J. "Catalytic Hydrodesulfurisation" Rev. Inst. Mex. Pet., **10**(4), 71-75, 1978.

Sanford, E.C.; Yui, S.M. "Hydrotreating Characteristics of Coked and of Hydrocracked Gas Oils with Commercial Nickel- Molybdenum Catalysts, and Prediction of Some Product Properties" Stud. Surf. Sci. Catal., 19 (Catal. Energy Scene), 585-592, 1984.

Sapre, A.V.; Gates, B.C. "Hydrogenation of Biphenyl Catalyzed by Sulfided $CaO-MoO_3/\gamma-Al_2O_3$. The Reaction Kinetics" Ind. Eng. Chem. Process Des. Dev., 21, 86-94, 1982.

Sasaki, Y.; Ojima, Y.; Kondo, T.; Ukegawa, K.; Matsumura, A.; Nakamura, E. "Hydrocracking of Heavy Oils with Fine Powder Catalysts. Part 7. Catalytic Activity of Heavy Oil Ashes" Sekiyu Gakkaishi, 26(2), 144-149, 1983a.

Sasaki, Y.;Ojima, Y.; Kondo,T.; Ukegawa, K.; Matsumura, A.; Nakamura, E., "Hydrocracking of Heavy Oils with Highly Dispersed Vanadium Catalyst" Sekiyu Gakkaishi, 26(6), 472-477, 1983b.

Satterfield, C.N. "Trickle-Bed Reactors" AIChE J., 21(2), 209-228, 1975.

Satterfield, C.N. "Heterogeneous Catalysis in Practice" Mc.Graw Hill, Inc, New York, 1980.

Satterfield, C.N.; Cocchetto, J.F., "Reaction Network and Kinetics of the Vapour Phase Catalytic Hydrodenitrogenation of Quinoline" Ind. Eng. Chem. Process Des. Dev., **20**, 53-62, 1981.

Satterfield, C.N.; Gultekin, S. "Effect of H_2S on the Gatalytic Hydrodenitrogenation of Quinoline" Ind. Eng. Process Des. Dev., **20**, 62-68, 1981.

Satterfield, C.N.; Ozel, F. "Direct Solid-Catalysed Reaction of a Vapour in an Apparently Completely Wetted Trickle-Bed Reactor" AIChE J., 19, 1259-1261, 1973.

Satterfield, C.N.; Roberts, G.W. "Kinetics of Thiophene Hydrogenolysis on a Co-Mo Catalyst" AIChE J., 14, 159-164, 1968.

Satterfield, C.N.; Smith, C.N.; Ingallo, M. "Catalytic Hydrodenitrogenation of Quinoline: Effect of Water and H_2S" Ind. Eng. Chem. Process Des. Dev., 24, 1000-1004, 1985.

Scamangas, A.; Papayannakos, N.; Marangozis, J. "Catalytic Hydrodesulfurisation of Petroleum Residue" Congr. Mediterr. Ing. Quim. (Actas), 2nd, D16-1/D 16-14, 1981.

Schneider, W.; Mueller, E.; Zschocke, R.; Onderka, E. "The Leuna Hydrocracking Process for Vacuum distillates. Part I. Composition, Conversion and Serviceabilty of Products" Chem. Tech. (Leipzig), 33(10), 508-511, 1981.

Schoengut, J.; Cir, J.; Eckert, E.; Marek, M. "Optimal Operation of Hydrodesulfurisation Reactor Based on a Kinetic Model" Acta Chim. Acad. Sci. Hung., 111(2), 189-197, 1982.

Schrader, G.L.; Cheng, C.P. "In Situ Laser Raman Spectroscopy of the Sulfiding of $Mo/\gamma-Al_2O_3$ Catalysts" J. Catal., 80, 369-385, 1983.

Schuetze, B.; Hofmann, H. "How to Upgrade Heavy Feeds" Hy. Proc., 63(2), 75-82, 1984.

Schuit, G.C.A.; Gates, B.C. "Chemistry and Engineering of Catalytic Hydrodesulfurisation" AIChE J., 19(3), 417-445, 1973.

Sedricks, W.; Kenney, C.N. "Partial Wetting in Trickle-Bed Reactors- The Reduction of Crotonaldehyde Over a Palladium Catalyst" Chem. Eng. Sci., 28, 559-568, 1973.

Shah, G.N.; Sherman, L.G.; Christ, M.A. "Residfining for Better

Fuel Oil" Hy. Proc., 58(5), 103-106, 1979.

Shih, S.S.; Milstein, D. "Low Pressure Cyclic Hydrocracking Process Using Multi-Catalyst Bed Reactor for Heavy Liquids" U.S. Patent U.S. 4,421,633, 1983.

Shipikin, V.V.; Bortov, V.Y.; Georgievskii, V.Y.; Zharkov, B.B.; Klimenko, T.M. "Preparation of High-Octane Gasoline Components by Catalytic Reforming and Selective Hydrocracking" Nefte Pererab. Neftekhim. (Moscow), 8, 3-5, 1983.

Shiroto, Y.; Nakata, S.; Fukui, Y.; Takeuchi, C. "Asphaltene Cracking in Catalytic Hydrotreating of Heavy Oils. 3. Characterisation of Products from Catalytic Hydroprocessing of Khafji Vacuum Residue" Ind. Eng. Chem. Process Des. Dev., 22, 248-257, 1983.

Shripek, M. "Upgrading Heavy California Crude to Low Sulfur Syncrude by the Unicracking/HDS Process" Future Heavy Crude Oils Tar Sands, Int. Conf., 1st 1979, 670-676, Pub. 1981.

Siewart, H.R.; Koenig, A.H.; Ring, T.A. "Optimize Design for Heavy Crude" Hy. Proc., 64(3), 61-66, 1985.

Sikonia, J.G. "New Data for RCD Unibon" Hy. Proc., 79(44), 126-139, 1981.

Sokolov, V.P.; Zaidman, N.M. "Kinetics and Selectivity of n-Heptane Transformation on Alumina-Platinum Catalyst Under Reforming Conditions" Kinet. Katal., 24(4), 898-903, 1983.

Sonnemans, J.W.M.; Plantenga, F.L.; Desai, P.H.; D'Amico, V.J.; Dixon, P.H. "Mild Hydrocracking of Heavy Oils in the Eighties" Natl. Pet. Refiners Assoc. (Tech. Pap.), AM-84-60, 31 pp, 1984.

Stefan, R.; Emig, G.; Hofmann, H., "On the Kinetics of Hydrodesulfurisation of Gas Oil" Chem. Eng. Process, 19(6),

303-315, 1985.

Steijns, M.; Froment, G.F. "Hydroisomerisation and Hydrocracking. 3. Kinetic Analysis of Rate Data for n-Decane and N-Dodecane" Ind. Eng. Chem. Prod. Res. Dev., 20, 660-668, 1981.

Steijns, M.; Froment, G.F.; Jacobi, P.; Uytherhoeven, J. "Hydroisomerisation and Hydrocracking. 2. Product Distribution for n-Decane and n-Dodecane" Ind. Eng. Chem. Prod. Res. Dev., 20(4), 654-660, 1981.

Steinberg, K.H.; Becker, K.; Nestles, K.H. "Hydroisomerisation and Hydrocracking Of n-Paraffins on Zeolite Catalysts" Acta. Phy. Chem., 31(1-2), 441-455, 1985.

Sue, H.; Sugiyama, H. "Hydrogenolysis of Heavy Oils" Petrotech (Tokyo), 5(10), 942-947, 1982.

Sullivan, R.F.; Egan, C.J., Langlois, G.E., "Hydrocracking of Alkylbenzenes and Polycyclic Aromatic Hydrocarbons on Acidic Catalysis Evidence for Cyclization of the Side Chains" J. Catal., 3(2), 183-195,1964.

Suzuki, M.; Shimada, K.; Kuriki, Y.; Ohshima, S.; Ohshima, S.; Takematsu, T., Kata, J.; Ohse, H. "Hydrodesulfurisation of Residual Oil by a Moving-Bed Reactor" Proc. Inst. Clean Air Congr., 4th, 735-738, 1977.

Swift, H.E.; Black, E.R. "Superactive Nickle-Aluminosilicate Catalysts for Hydroisomerisation and Hydrocracking of Light Hydrocarbons" Ind. Eng. Chem. Prod. Res. Dev., 13, 106-109, 1974.

Takemura, Y.; Itoh, H.; Ouchi, K., "Catalytic Hydrodesulfurisation of Residual Oil by a Mixture of CO and H_2O" Sekiyu Gakkashi, 24(6), 357-362, 1981.

Takeuchi, C.; Fukui, Y.; Nakamura, M.; Shiroto, Y. "Asphaltene Cracking in Catalytic Hydrotreating of Heavy Oils. 1. Processing

of Heavy Oils by Catalytic Hydroprocessing and Solvent Deasphalting" Ind. Eng. Chem. Process Des. Dev., **22**, 236-242, 1983.

Teichman, D.P.; Bridge, A.G.; Reed, E.M. "Building to Handle More Resid" Hy. Proc., **61**(5), 105-109, 1982.

Togari, O.; Matsuda, M.; Shimokawa, K.; Makabe, T. "Catalyst and Method for Hydrocracking of Heavy Hydrocarbon Oils" Ger. Offen. Patent DE 3,321,485, 1983.

Topsoe, H.; Clausen, B.S. "Importance of Co-Mo-S Type Structures in Hydrodesulfurisation" Catal. Rev. Sci. Eng., **26**(3-4), 395-420, 1984.

Topsoe, H.; Clausen, B.S.; Clausen, B.S., Topsoee, N.Y.; Petersen, E. "Recent Basic Research in HDS Catalyst" Ind. Eng. Chem. Fundam., **25**(1), 25-36, 1986.

Treese, S.A.; Murphy, J.R., API Meeting, San Francisco, Calif., 1978.

Ukegawa, K.; Ojima, T.; Kondo, T.; Matsumura, A.; Sakabe, T.; Yobori, H.; Konishi, H. "Hydrocracking of Heavy Oils with Fine Powder Catalysts. 4. Hydrocracking of Residual Oil with a Catalyst from Desulfurisation Plant" Sekiyu Gakkaishi, **23**(4), 280-286, 1980.

Vail, Y.K.; Manshilin, V.V.; Lipkind, B.A.; Agafanov, A.V.; Kuyazev, V.S. "Hydrodesulfurisation of Petroleum Residues with Preliminary Hydrodemetallization" Khim. Tverd. Topl. (Moscow), **6**, 128-131, 1980.

van Deemter, J.J. "Trickle HDS - A Case History" 3rd. Eur. Symp. Chem. React. Eng., Pergamon Press, Oxford, 215-223, 1965.

van Dongen, R.H.; van der Eijk, H.; Bode, D.; van Klinken, J. "Hydrodemetallation of Heavy Residual Oils in Laboratory

Trickle-Flow Liquid Recycle Reactors" Ind. Eng. Chem. Process Des. Dev., **19**, 630-635, 1980.

van Driesen, R.P.; Caspers, J.; Campbell, A.R.; Lumin, G. "L.C. Fining Upgrades Heavy Crude" Hy. Proc., 58(5), 107-111, 1979.

van Klinken, J.; Pronk, K.M.A. "Process for Desulfurisation of Hydrocarbon Oils" Brit. 1,525,508, 1978.

van Parijs, I.A.; Froment, G.F. "Kinetics of Hydrodesulfurisation on a Co-Mo/γ-Al$_2$O$_3$ Catalyst 1. Kinetics of the Hydrogenolysis of Thiophene" Ind. Eng. Chem. Prod. Res.Dev., 25, 431-436, 1986.

van Parijs, I.A.; Hosten, L.H.; Froment, G.F. "Kinetics of Hydrodesulfurisation on a Co-Mo/γ-Al$_2$O$_3$ Catalyst. 2. Kinetics of Hydrogenolysis of Benzothiophene" Ind. Eng. Chem. Prod. Res. Dev., **25**, 437-443, 1986.

Vansina, H.; Baltanos, M.A.; Froment, G.F. "Hydroisomerisation and Hydrocracking. 4. Product Distribution from n-Octane and 2,2,4-Trimethyl Pentane" Ind. Eng. Chem. Prod. Res. Dev., **22**, 526-531, 1983.

Vecchi, C.; Marengo, S.; Iannibello,, A.; Girelli, A. "Surface Structure and Functionality of Bauxite- Based catalyst in the Hydrotreating of Heavy Crudes" prep. - Am. Chem. Soc., Div. Pet. Chem., **27**(3), 732-741, 1982.

Voorhies Jr., A.; Smith, W.M. "Advances in Hydrocracking" Advan. Pet. Chem. and Refining, vol. VIII, Ed. McKetta Jr., J.J., Interscience, New York, 169-191, 1964.

Vrinat, M.L. "The Kinetics of the Hydrodesulfurisation Process- A Review" Appl. Catal., 6(2), 137-158, 1983.

Waugh, R.J.; Chambers, L.W.; Menzies, M.A.; Patmore, D.J. "CANMET Hydrocracking Handles Wide Range of Heavy Crude" Natl. Pet. Refiners Assoc. (Tech. Pap.), AM-83-44, 1983.

Ward, J.W.; Hansford, R.C.; Reichte, A.D.; Sosnowski, J. "Catalyst Advances Open Door for Hydrocracking" O & G J., **71(22)**, 69-73, 1973.

Yan, Y.Y. "Dynamics of a Trickle-Bed Hydrocracker with a Quenching System" Can. J. Chem. Eng., 58(2), 259-266, 1980.

Yan, Y.Y. "Zeolite-Based Catalyst for Hydrocracking" Ind. Eng. Chem. Process Des. Dev., **22**, 154-160, 1983.

Yang, S.H.; Satterfield, C.N. "Catalytic HDN of Quinoline in a Trickle-Bed Reactor. Effect of H_2S" Ind. Eng. Chem. Process Des. Dev., **23**, 20-25, 1984.

Yitzhaki, D.; Aharoni, C. "Hydrodesulfurisation of Gas Oil Reaction, Rates in Narrow Boiling Range Fractions" AIChE J., **23**, 342-346, 1977.

Yulin, M.K.; Meged, N.F.; Golovchenco, S.V.; Mezhlu'mova, A.I.; Arifulin, A.S. "Hydrogenation of Thiophene on Zeolite Catalysts" Khim. Tverd. Topl. (Moscow), (1), 85-88, 1988.

Zhorov, Y.M.; Panchenkov, G.M.; Tatarintseva, G.M.; Rogov, S.D.; Agafonov, A.V.; Khavkin, V.A. "Mathematical Modeling of the Hydrocracking and Hydrodesulfurisation of Petroleum Residues for the Production of Boiler Fuels" Nauchn. Osn. Pererab. Nefti Gaza Neftekhim., Tezisy Dokl., Vses. Konf., 13, 1977.

Zingg, D.S.; Makovsky, L.E.; Tischer, R.E.; Broun, F.R.; Hercules, D.M. "Exoelectron Emission from Aluminium under the Influence of Applied Electric Potential and Stimulating Light, and Its Dependence on Surface-Polar Organic Interaction" J. Phys. Chem., **84**, 2898-2906, 1980.

CHAPTER - 3

MODELING OF A HYDROCRACKING REACTOR

3.1 INTRODUCTION

The rapid increase in the demand for diesel-kerosene fractions has resulted in the development of many new processes which can convert the heavier petroleum fractions into more usable lighter products. Earlier, hydrogenation processes were not widely used because of unfavourable economic conditions, but with tremendous growth of catalytic reforming and resulting quantities of hydrogen as by-product, hydrogenation processes have become economically attractive. Hydrocracking was one of the earliest applications of hydrogenation and is of current interest because of its extreme versatility to process a variety of difficult feedstocks to a wide spectrum of desirable products.

Mathematical modeling provides a tool to better understand the process in addition to its use for process optimization and control. For a model to predict the reactor outlet concentration and temperature accurately from the reactor inlet concentrations, flows and reactor dimensions, the set of equations constituting the model should represent the actual physical system as closely as possible. These models are useful in improving the existing plant operation and in scaling up of pilot plants. Some of the models for hydrocrackers published in the literature have been summarised in Section 2.1.5

Three-phase reactors (gas-solid-liquid) of trickle-bed type are widely used for hydrocracking of vacuum gas oil (VGO). A two-stage hydrocracker with recycle is more common nowadays. The first stage primarily removes the sulfur and nitrogen compounds and in the second stage, hydrocracking takes place. Hydrocracking of VGO consists of several simultaneous and consecutive reactions. Since petroleum oil is a complex mixture of organic compounds, it is difficult to separately account for each component present in the mixture. Hence the published models consider only a few pseudo-components which best represent the feed. Numerous studies on product distribution during hydrocracking of n-alkanes have been reported but these provide little information on hydrocracking of petroleum fractions. Stangeland (1974) has, however, given some empirical correlations for predicting the yield from a hydrocracker for petroleum fractions. A more recent work on predicting the yield from a hydrocracker has been reported by Krishna and Saxena (1989).

In this study a mathematical model for a two-stage VGO hydrocracking unit with intermediate gas quenching between the catalyst beds is presented. A simplified schematic process flow sheet for a VGO hydrocracker is shown in Figure 3.1. The feed was a mixture of vacuum gas oils from different crudes. The TBP cut range of the feed to the first stage was 753 - 838 K. The effluent from the first stage was fractionated and the fractions having boiling point above 753 K were fed to the second stage. The effluent from the second stage was also fractionated and the fractions boiling above 753 K were again recycled to the second stage. The first stage reactor consisted of four catalyst beds with intermediate hydrogen quenching. The second stage reactor
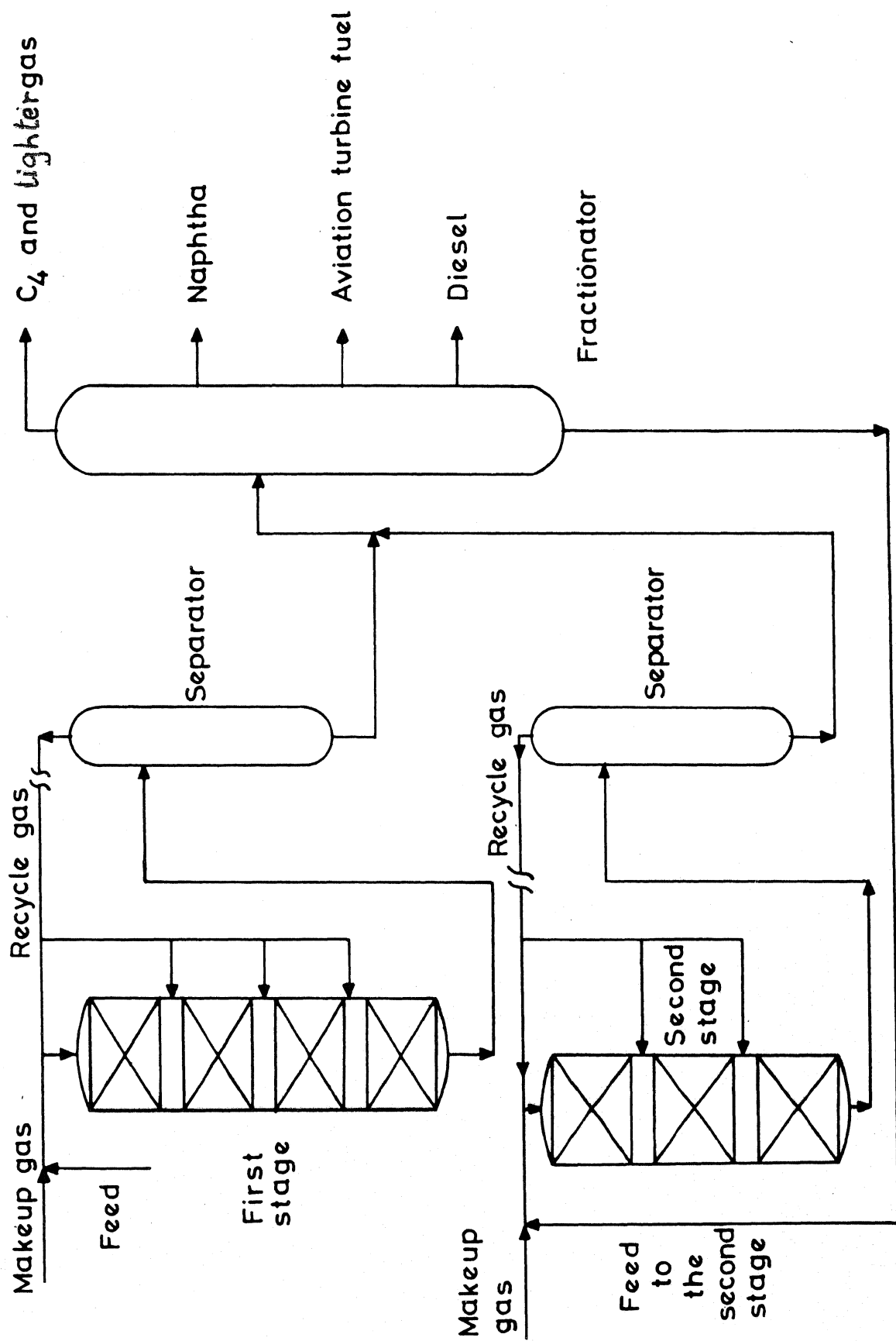
Fig. 3.1 A simplified schematic diagram for VGO hydrocracking unit.

consisted of three catalyst beds with intermediate quenching (Figure 3.1). Both the reactors used the same type of catalyst. The specifications of the feed to the first stage are given in Table 3.1.

3.2 MODEL DEVELOPMENT

The model for a trickle-bed reactor consists of a set of ordinary differential equations (ODE) and a set of procedures which incorporate the algebraic equations. The ODE include the mass and heat balance equations whereas the algebraic equations are the physical and thermodynamic properties correlations.

The following assumptions have been made in the development of the present model:

(i)   hydrocracking is a first order pseudo-homogeneous reaction. Since hydrogen is present in excess, the change in the hydrogen concentration is insignificant and the rate of hydrocracking can be taken to be independent of the hydrogen concentration. A first order rate expression has been reported by several authors (Qader and Hill, 1969; Stangeland, 1974; El Kady, 1979).

(ii) plug flow pattern reactor. Satterfield (1975) has reported that the flow pattern in trickle-bed is close to that of plug flow.

(iii) heat losses are negligible. It has been reported in the literature (Satterfield, 1975) that the commercial reactors are generally designed to operate under adiabatic conditions.

(iv) no diffusional resistances. Similar assumption has also been reported by other investigators (Scot and Bridge,

TABLE 3.1 Plant Data for VGO Hydrocracking Unit

TBP cut point,K	643-838
Gravity, °API	27
Specific gravity at 288.6K/288.6K	0.8927
Total Sulfur, wt %	1.44
Nitrogen, ppm	500
Conradson Carbon	0.32
Asphaltene content, ppm	<100
Charaterisation Factor	12.2
Anilin Point, K	364

D1160 Distillation, K

IBP	593
5%	643
10%	658
30%	688
50%	716
70%	741
90%	781
95%	798
100%	838

	1st stage	2nd stage
Total feed rate, m^3/h	227	202
Catalyst type	ICR 106	ICR 106
Total catalyst volume,m^3	160	150
Active catalyst volume,m^3	149.5	150
Reactor inlet pressure,kg/cm^2 g	178	174
Reactor inlet temperature, K	672	644
Reactor outlet temperature, K (maximum)	714	700
Recycle gas rate, Nm^3/h	270,000	157,000
Reactor feed gas rate, (Nm^3/m^3 feed)	800	800
make-up gas, Nm^3/h	42350	21400

1971; Gerdes et al., 1977).

(v) steady state operation.

(vi)   recycle and make-up gases are pure hydrogen.

(vii)   the petroleum feed and the products are in the liquid phase in the reactor.

(viii) the summation of the product of the total mass flow rate and its heat capacity is constant for each catalyst bed.

The present study makes use of Stangeland's model (1974) for predicting the yield from a hydrocracker since it is the only available model in the published literature which deals with the product distribution of petroleum fractions during hydrocracking. The concept of pseudo-components has been incorporated to divide the wide boiling range VGO into groups of narrow boiling fractions. Each fraction or pseudo-component was characterised by its true mid-boiling point and in this study the boiling range interval, was taken to be 25 K. Similar to Stangeland's model (1974), it has been assumed that the products formed from cracking of any fraction range from butanes (having a boiling range from 263 to 288 K) to a pseudo-component having a boiling point 50 K less than the fraction being cracked. The product distribution is predicted by empirical correlations. Since this model does not differentiate between the different hydrocarbon types boiling in the same temperature interval, it cannot predict the detailed composition of each pseudo-component. As the rate of cracking decreases with decrease in molecular weight, it has been assumed that the components having a boiling point less than 400 K do not crack. Polymerisation reactions, leading to products heavier than the component being cracked, were neglected. These reactions are generally insignificant.

Based on the above assumptions, the hydrocracking reaction can be represented by the following scheme:

$$A_N \xrightarrow{H_2} A_1 + A_2 + A_3 + - - - - +A_{N-2}$$

$$A_{N-1} \xrightarrow{H_2} A_1 + A_2 + A_3 + - - - - - + A_{N-3} \qquad (3.1)$$

$$A_i \xrightarrow{H_2} A_1 + A_2 + A_3 + - - - - - +A_{i-2}$$

$$A_6 \xrightarrow{H_2} A_1 + A_2 + A_3 + A_4$$
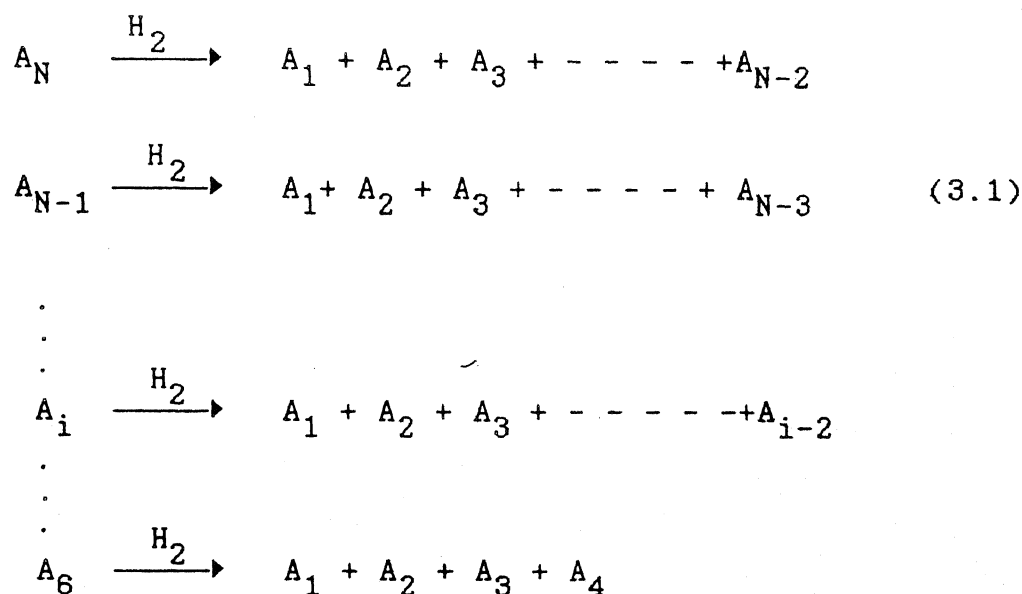
where A_i is the component undergoing cracking. $A_1, A_2, \ldots, A_{i-2}$ are the products formed from cracking of A_i, of which products with $i \geq 6$ undergo further hydrocracking to give still lighter products. In a similar manner all the pseudo-components having boiling points above 400 K (boiling point of A_6 is 400.5 K) undergo cracking. The component numbers $1, 2, \ldots, N$ are in ascending order of boiling range and consequently, molecular weight; the heaviest pseudo-component being A_N. It may be noted that all the pseudo-components undergoing hydrocracking need not be present in the feed. In the present case, the feed consisted of components from A_{23} to A_{13}, whereas the product contained pseudo-components ranging from A_{23} to A_1.

The critical properties and the molecular weights of the pseudo-components were estimated using the Lee-Kesler's

correlations (Lee and Kesler, 1975; Kesler and Lee, 1976) which are given as functions of specific gravity and boiling point. The thermodynamic properties were predicted using Peng-Robinson's equation of state (EOS) the details of which are given in Section 3.2.4.

3.2.1 Material Balance Equations

The component differential mass balance equations for the liquid phase in the trickle bed reactor can then be represented by

$$M_t dC_i/dW = - k_i C_i + \sum_{j=r}^{N} k_j P_{ij} C_j$$

$$(3.2)$$

$$\text{for } i = 1,2,\ldots,N$$

$$r = i+2 \quad \text{for } i \geq 5$$

$$= 6 \quad \text{for } i < 5$$

where C_i represents the concentration of ith pseudo-component. The first term on the right hand side of Eqn. (3.2) represents the rate of disappearance of the ith pseudo-component, whereas the second term represents the rate of formation of the same pseudo-component from components heavier than itself. The liquid mass flow rate is assumed to be constant along the reactor. k_i is the first order rate constant having the units (kg reactant)/(kg catalyst)(h). P_{ij} is the probability of the ith pseudo-component being formed from the jth pseudo-component and is estimated using correlations similar to those of Stangeland (1974). Since the rate of hydrocracking has been assumed to be independent of hydrogen concentration, the component balance for hydrogen was not necessary. The overall hydrogen consumption was, however,

calculated using a procedure discussed in Section 3.3.1.

3.2.2 Energy Balance Equation

The energy balance across a differential catalyst mass element leads to the following ODE.

$$dT/dW = \sum_j (-\Delta H_R)_j k_j C_j / \sum_i m_i Cp_i \qquad (3.3)$$

$$i = 1, - - - , N+1$$
$$j = p, - - - , N$$

In the above equation, both the gas phase as well as the liquid phase components have been included. The (N+1)th component is the gas phase component (ie. hydrogen). $(\Delta H_R)_j$ is the heat of reaction for hydrocracking of component j, m_i is the mass flow rate of component i, Cp_i is the heat capacity of component i, T is the temperature and p is the lightest component undergoing cracking.

3.2.3 Correlations for Predicting P_{ij} and k_i :

The product distribution during hydrocracking of n-alkanes over different types of catalysts has been studied by several authors (Archibald et al.,1960; Flinn et al.,1960; Coonradt and Garwood,1964; Goldfarb et al.,1981; Langlois and Sullivan,1970; Steijn et al.,1981; Vansina et al.,1983) but these results are not directly applicable to petroleum fractions. However, Stangeland (1974) has developed some correlations which were used for predicting the product distribution during hydrocracking of Raw California Gas Oil in a two-stage reactor. In his study the product distribution was correlated as a function of two parameters.

During the hydrocracking of each pseudo-component, some butanes and lighter fractions are formed. An expression similar to that given by Stangeland (1974) was used for evaluating the mass fraction of butanes and lighter components in the product formed by hydrocracking of pseudo-component j (P_{1j}) and is:

$$P_{1j} = C \exp \{ -0.00693(1.8tb_j - 229.5)\} \qquad (3.4)$$

where tb_j is the boiling point of pseudo-component j in ^oC and C is a constant which depends on the type of feed and catalyst used. The yield of all other fractions having boiling points higher than that of the butanes were evaluated using one common expression. The entire product boiling point range, ie. starting from the boiling point of the fraction just heavier than the butanes to the boiling point of the heaviest product formed, was first normalised. The normalisation equation was

$$y_{ij} = \frac{(tb_i - 2.5)}{[(tb_j - 50)-2.5]} \qquad (3.5)$$

$$i = 2,\ldots,j-2$$
$$j = 6,\ldots,N$$

where y_{ij} is the normalised temperature for the ith product formed from jth pseudo-component. The product distribution could then be calculated using the expression

$$P'_{ij} = [y_{ij}^2 + B(y_{ij}^3 - y_{ij}^2)][1-P_{1j}] \qquad (3.6)$$

where P'_{ij} is the cumulative yield till the ith pseudo-component from hydrocracking of the jth pseudo-component. The actual yield

of the pseudo-component i from component j was then obtained by subtracting $P'_{i-1,j}$ from P'_{ij}, ie.

$$P_{ij} = P'_{ij} - P'_{i-1,j} \qquad (3.7)$$

The shape of the product distribution curve depends on the parameter B which generally varies from -2 to 1. When B = 0, the product distribution is linear. For B=-2, the probability of the molecule breaking into two equal halves is a maximum. The parameters,B and C depend on the paraffin content in the feed and the type of the catalyst.

The rate constant ,k_i, is highly dependent on the type of hydrocarbons. For instance, the rate of cracking of n-paraffins is less than the rate of cracking of aromatics, cycloparaffins and isoparaffins of the same carbon number. Several kinetic studies on hydrocracking of n-paraffins and some petroleum oils have been published, but their application becomes limited because of the different reaction conditions and the catalyst used. The size, shape and past history of the catalyst are also likely to affect the reaction rate. In the absence of an appropriate rate equation, generally the simplest form of rate expression is assumed. In the present model, the individual rate constants for the pseudo-components were calculated by developing a relative rate function together with an estimated value of the absolute rate constant of a mixture with an average boiling point of 638 K. Qader and Hill (1969) have reported a first order rate expression for hydrocracking of a vacuum gas oil having an average boiling point of 638 K (boiling range: 573-703 K) as

$$k = 1.0 \times 10^7 \, e^{-21100/RT} \qquad\qquad (3.8)$$

where k is the rate constant given in (vol. feed)/(vol. cat)(h), R is in kcal/(kmol)(K) and T, the reactor temperature is in K. As a first estimate it was assumed that a fraction with an average boiling point of 638 K had the same rate constant as given by Eqn. (3.8). This was later adjusted to minimize the deviation between the calculated and measured yields.

The relative rate function was developed based on the results of Rapaport (1962) who reported relative rates for hydrocracking of normal alkanes and found that the rate increased in the ratio $1/32/72/120$ for $C_5/C_{10}/C_{15}/C_{20}$. The following polynomial expression gave the best fit to the plant data:

$$K_i' = 0.494 + 0.52 \times 10^{-2} \, tb_i - 2.185 \times 10^{-5} tb_i^2 + 0.312 \times 10^{-7} tb_i^3$$

$$(3.9)$$

where tb_i is the boiling point of the ith pseudo-component in $^{\circ}C$ and K_i' is its relative rate constant. The rate constant for component i, k_i, could then be calculated as

$$k_i = k \, K_i' \qquad\qquad (3.10)$$

3.2.4 Evaluation of Thermodynamic Properties

The estimation of thermodynamic properties such as heat capacity, enthalpies etc. are necessary to account for the heat

effects and calculate equilibrium composition of the reaction mixture. Several group contribution methods for predicting these properties for pure hydrocarbons are available (Reid et al., 1977), but since the detailed chemical composition of the petroleum oil was not known, none of these methods could be used. The empirical relations given by Lee and Kesler (1975) and Kesler and Lee (1976) for molecular weight (MW), critical pressure (P_c), critical temperature (T_c), critical volume (V_c), acentric factor (ω) and compressibility factor (Z_c) for petroleum fractions as a function of normal boiling point (Tb) and specific gravity (SG) have been used in the present model and are given below:

For a pure component i :

$$MW_i = -12272.6 + 9486.4SG_i + (4.6523 - 3.3287SG)Tb_i$$

$$+ (1 - 0.77084SG_i - 0.02058SG_i^2)(1.3437 - 720.79/Tb_i)10^7/Tb_i$$

$$+ (1 - 0.80882SG_i + 0.02226SG_i^2)(1.8828 - 181.98/Tb_i)10^{12}/Tb_i^3$$

$$(3.11)$$

$$\ln P'_{ci} = 8.3634 - 0.0566SG_i - (0.24244 + 2.2898/SG_i + 0.11857/SG_i^2)$$

$$10^{-3}Tb_i + (1.4685 + 3.648/SG_i + 0.47227/SG_i^2)$$

$$10^{-7}Tb_i^2 - (0.42019 + 1.6977/SG_i^2)10^{-10}Tb_i^3$$

$$(3.12)$$

$$T_{ci} = 341.7 + 811SG_i + (0.4244 + 0.1174SG_i)Tb_i$$

$$+ (0.4669 - 3.2623SG_i)10^5/Tb_i \qquad (3.13)$$

$$\omega_i = \frac{-\ln P_{ci} - 5.92714 + 6.09648/Tb_{ri} + 1.28862 \ln Tb_{ri} - 0.169547 Tb_{ri}^6}{15.2518 - 15.6875/Tb_{ri} - 13.47211 \ln Tb_{ri} + 0.43577 Tb_{ri}^6}$$

(3.14)

$$Z_{ci} = 0.2905 - 0.085 \omega_i \qquad (3.15)$$

$$V_{ci} = \frac{Z_{ci} R T_{ci}}{P_{ci}} \qquad (3.16)$$

where Tb_{ri} is the reduced normal boiling point of component i.

For a mixture :

$$V_{cm} = \frac{1}{8} \left(\sum_{i=1}^{N} \sum_{j=1}^{N} x_i x_j (V_{ci}^{1/3} + V_{cj}^{1/3})^3 \right) \qquad (3.17)$$

$$T_{cm} = \frac{1}{8V_{cm}} \left(\sum_{i=1}^{N} \sum_{j=1}^{N} x_i x_j (V_{ci}^{1/3} + V_{cj}^{1/3})^3 (T_{ci} T_{cj})^{1/2} \right) \qquad (3.18)$$

where the subscript m refers to the mixture critical properties. The correlations available for predicting the heat capacities of the components (Lee and Kesler, 1975 and Kesler and Lee ,1976) were not applicable to this system because of severe reaction conditions. The modified form of Lee-Kesler's equation (Yu et al.,1982) was not used because it would have to be solved iteratively and since there are a large number of components it could have consumed a lot of computer time. Hence, Peng Robinson's cubic EOS (1976) was used to calculate the enthalpy of pure

components as well as those of mixtures (Walas,1985).

Peng Robinson's EOS :

For pure components :

$$Z^3 + (B-1)Z^2 + (A - 3B^2 - 2B)Z - (AB - B^2 - 3B) = \emptyset$$

<div align="right">(3.19)</div>

where ,

$$A = \alpha a P_t / R^2 T^2$$

$$B = b P_t / RT$$

$$a = 0.45724 R^2 T_c^{\,2} / P_c$$

$$b = 0.0778 RT_c / P_c$$

$$\alpha = (1 + (.37464 + 1.54226\omega - .26992\omega^2)(1 - Tr^{0.5}))^2$$

Z is the compressibility factor, P_t is the total pressure in atm and R is in $(m^3)(atm)/(kmol\ K)$.

For a mixture :

$$a\alpha = \sum_{i=1}^{N} \sum_{j=1}^{N} x_i x_j (a\alpha)_{ij} \qquad \text{where i and j refer to the component number}$$

$$(a\alpha)_{ij} = (1 - k_{ij}) \sqrt{(a\alpha)_i (a\alpha)_j}$$

$$A = \sum_{i=1}^{N} \sum_{j=1}^{N} x_i x_j A_{ij}$$

$$B = \sum_{i=1}^{N} x_i B_i$$

$$A_{ij} = (1 - k_{ij}) A_i A_j$$

where k_{ij}'s are the interaction parameters. Due to lack of data k_{ij}'s were assumed to be zero for all the components.

The cubic EOS can be solved for Z analytically using the method given in Chemical Engineers' Handbook (Perry and Green, 1984). The fugacity coefficient, defined as the ratio of the fugacity of a material to its pressure can readily be calculated from the PVT data.

For a pure substance, the fugacity coefficient based on Peng Robinson's EOS is,

$$\ln \emptyset = (Z-1) - \ln(Z-B) - \frac{A}{4.828} \ln \frac{(Z + 2.414B)}{(Z - .414B)} \tag{3.20}$$

The partial fugacity coefficient, $\hat{\emptyset}_i$, or the fugacity coefficient of a component in solution is given by

$$\ln \hat{\emptyset}_i = \frac{B_i}{B} (Z-1) - \ln(Z-B) + \frac{A}{4.828B} \left(\frac{B_i}{B} - \frac{2}{a\alpha} \sum_j x_j (a\alpha)_{ij}\right)$$

$$\ln\left(\frac{Z + 2.414B}{Z - 0.414B}\right) \tag{3.21}$$

The excess enthalpy, $H_i'^{ex}$, for a pure component i is related to its fugacity co-efficient ($\emptyset_i$) by the thermodynamic relation

$$H_i'^{ex} = H_i' - H_i'^{idl} = - RT^2 \frac{\partial \ln \emptyset_i}{\partial T} \tag{3.22}$$

$$H_i^{ex} = \frac{H_i'^{ex}}{(MW)_i} \tag{3.22a}$$

where H_i' is the enthalpy of the ith component in kJ/kmol at any temperature T, H_i^{ex} is the excess enthalpy of component i in kJ/kg and R has the units kJ/(kmol)(K). The excess enthalpy for a mixture $(H_m'^{ex})$ is related to the partial fugacity coefficient by the following relation

$$H_m'^{ex} = H_m' - H_m'^{idl} = -RT^2 \sum [(\partial \ln \hat{\phi}_i)/\partial \, . \, T] \qquad (3.23)$$

$$H_m^{ex} = \frac{H_m'^{ex}}{(MW)_m} \qquad (3.23a)$$

where H_m' is the enthalpy of the mixture, $H_m'^{idl}$ is the ideal gas enthalpy of the mixture having the units kJ/kmol and H_m^{ex} is the excess enthalpy for the mixture in kJ/kg. The ideal gas enthalpy, $H_i'^{idl}$, is calculated using the correlation given by Weir and Eaton (1932) for enthalpy of vapour above 273 K and low pressures. Gary and Rubin (1933) found that the correlation was satisfactory for practically all types of feedstocks. The equation is given below for a component i

$$H_i^{idl} = 2.32[(215 - 87SG_i) + (0.415 - 0.104SG_i)t'$$
$$+ (0.00031 - 0.000078SG_i)t'^2]$$

$$(3.24)$$

$$H_i'^{idl} = (MW)_i \, H_i^{idl} \qquad (3.24a)$$

$$H_m^{idl} = \sum C_i \, H_i^{idl} \qquad (3.25)$$

$$H_m'^{idl} = \sum y_i' \, H_i'^{idl} \qquad (3.25a)$$

where H_i^{idl} is the total heat above 273 K, kJ/kg

$H_i^{'idl}$ is the total heat above 273 K, kJ/kmol

SG_i is the specific gravity at 288.6 K

t' is the temperature in ^oF and

C_i is the mass fraction of component i.

y_i' is the mole fraction of component i

$H_m^{'idl}$ is the total heat above 273 K for a mixture, kJ/kmol

H_m^{idl} is the total heat above 273 K for a mixture, kJ/kg

Thus H_i' can be obtained from Eqns (3.22) and (3.24) and H_m' from Eqns. (3.23) through (3.25). The heat capacity of the component i (Cp_i') and of a mixture (Cp_m') can be obtained from Eqns. (3.26) and (3.27) respectively.

$$Cp_i' = H_i' / (T - 273) \qquad (3.26)$$

$$Cp_i = \frac{Cp_i'}{(MW)_i} \qquad (3.26a)$$

$$Cp_m' = H_m' / (T - 273) \qquad (3.27)$$

$$Cp_m = \frac{Cp_m'}{(MW)_m} \qquad (3.27a)$$

where Cp_i' and Cp_m' are in kJ/(kmol)(K) and Cp_i and Cp_m are in kJ/(kg)(K).

3 2.5 Heats of reaction

The heats of reactions for this system could not be calculated using the standard heats of combustion because of the undefined composition of the reaction mixture. One of the methods for estimating the standard heats of reactions for petroleum

fractions is based on the use of available heats of combustion data. However, the available heats of combustion data are also not very reliable (API Technical Data Handbook, 1977). In the present model, the heat of reactions were calculated on the basis of hydrogen consumed in each reaction. During the saturation of an aromatic double bond approximately 58-67 MJ and during cracking of a paraffin or naphthene, 29-42 MJ of heat is released per kmol of hydrogen consumed (Jaffe, 1976). Assuming that the feed consists mainly of paraffins and naphthenes, the heat released during any reaction has been taken to be 42 MJ/ kmol of hydrogen consumed at standard conditions. This agrees well with the calculated value of 42 MJ/ kmol of hydrogen consumed as standard heat of reaction for hydrocracking of normal hexadecane using the available heats of combustion data (Smith and Vanness, 1984). To estimate the hydrogen consumption, the carbon-to-hydrogen (C/H) ratio of each pseudo-component and the values of P_{ij}s are required. Since the methods for estimation of C/H ratio (R′) are not very reliable, two methods were used and the average value taken for calculating the hydrogen consumption. In one method, knowing the specific gravity and the average boiling point of the pseudo-component, the C/H ratio could be obtained from a nomograph (API Technical Data Handbook, 1977). In the second method, the tabulated data of Nelson (1958) were utilized, where C/H ratio was given as a function of UOP characterisation factor. Some extrapolation was necessary to cover the entire temperature range.

For hydrocracking of each pseudo-component, the mass of hydrocarbon required for unit mass of product can be calculated by the following method. The mass of the product i formed from pseudo-component j is represented by P_{ij} and the C/H ratio of

component i, by R_i'. Therefore, the total carbon content in the products formed from component j can be written as

$$(TWC)_j = \sum_{i=1}^{j-2} P_{ij} \frac{R_i'}{R_i'+ 1} \qquad (3.28)$$

$$j = 6,\ldots,N$$

which is also the carbon content of pseudo-component j ($W_{c,j}'$). The hydrogen content in the products formed from the component j can be written as

$$(TWH)_j = \sum_{i=1}^{j-2} P_{ij} \frac{1}{R_i'+ 1} \qquad j = 6,\ldots,N \qquad (3.29)$$

and the hydrogen content of pseudo-component j is given by

$$W_{H2,j}' = \frac{W_{c,j}'}{R_j'} \qquad j = 6,\ldots,N \qquad (3.30)$$

Therefore, the total mass of the hydrocarbon $(TR)_j$

$$(TR)_j = W_{c,j}' + W_{H2,j}' \qquad j = 6,\ldots N \qquad (3.31)$$

Thus, the hydrogen consumption for each reaction per unit mass of products, $(H_2C)_j$, is given by

$$(H_2C)_j = [(TWH)_j - W_{H2,j}'] \qquad j = 6,\ldots N \qquad (3.32)$$

Therefore the hydrogen consumption per unit mass of hydrocarbon

can be written as

$$(H_2CR)_j = (H_2C)_j / (TR)_j \qquad j = 6,\ldots,N \qquad (3.33)$$

Hence the standard heat of reaction for the jth reaction, $(\Delta H_R^o)_j$ is expressed as

$$(\Delta H_R^o)_j = (H_2CR)_j \ (-42) \ 10^3/ 2 \qquad kJ \ / \ kg \ hydrocarbon$$

$$j = 6,\ldots N \qquad (3.34)$$

To account for the effect of temperature and pressure on the heat of reaction, the enthalpy of the reactants and the products at reaction temperature and pressure, H_i, was estimated using the Peng-Robinson's EOS and at reference conditions, H_i^o, using the correlation given in Eqn. (3.35) formulated by Zhvanestskii and Platnov (Walas,1985) for liquid hydrocarbon mixtures.

$$H_i^o = \frac{4.18}{(MW)_i} \left(\frac{0.3897t + 0.0004638t^2}{\rho_i^{2/3}} \right) \left(0.3265 + \frac{0.4515}{\rho_i} \left(\frac{Tb_i}{273.2} +1 \right)^{1/3} \right)$$

$$(3.35)$$

where H_i^o is in kJ/kg, t is the temperature in ^oC, and ρ_i is the density in gm/ml for component i. For butanes and lighter hydrocarbons, which are not in the liquid state at the reference conditions, the enthalpy was calculated from the heat capacity of butanes (Cp_1') given by the following equation (Reid et al., 1977)

$$Cp_1' = [2.266 + 7.913 \times 10^{-2}T - 2.6475 \times 10^{-5}T^2 - 0.674 \times 10^{-9}T^3]4.18$$

$$(3.36)$$

$$Cp_1 = \frac{Cp'_1}{(MW)_1} \qquad (3.36a)$$

where T is in K and Cp'_1 in kJ/(kmol)(K) and Cp_1 is in kJ/(kg)(K). The enthalpy of hydrogen at reaction conditions (H_{H2}) as well as at standard conditions (H^o_{H2}) were calculated from the available heat capacity data (Vargaftik, 1975). The heat of reaction at reaction condition, $(\Delta H^T_R)_j$, can be finally written as

$$(\Delta H^T_R)_j = (\Delta H^o_R)_j + [\sum_{i=1}^{j-2} H_i\, P_{ij} - \{(TR)_j\, H_j + (H_2C)_j \times H_{H2}\}]/ (TR)_j$$

$$- [\sum_{i=1}^{j-2} H^o_i\, P_{ij} - \{ (TR)_j\, H^o_j + (H_2C)_j \times H^o_{H2}\}]/ (TR)_j$$

$$j = 6,\ldots, N$$

$$(3.37)$$

The set of equations from Eqn (3.1) to (3.37) form the mathematical model for the hydrocracking reactor. The total number of equations depends on the number of pseudo-components.

3.3 APPLICATION OF THE MODEL

The above developed model was used to calculate the yield of various products, hydrogen consumption and the reactor temperature profile for the VGO hydrocracker, the plant data for which are given in Table 3.1. The various parameters such as C and B in Eqns (3.4) and (3.6), respectively, and k in Eqn. (3.10) for the reference pseudo-component which had a boiling point of 638 K were varied to obtain the best fit with the plant yields. After several trials, it was found that for B=0.7 and C=0.37, the deviations between the calculated and plant yields were minimum.

Similarly optimum expression for k for the reference component was found to be

$$k = 0.9906 \times 10^7 \, e^{-10620/T} \text{ for the first stage and}$$

(3.38)

$$k = 0.7844 \times 10^7 \, e^{-10620/T} \text{ for the second stage.}$$

(3.39)

The pre-exponential term in the expression given by Qader and Hill (Eqn. 3.8) is 1.2, when the rate constant is expressed in units kg feed/(kg catalyst)(h). The same values for the parameter B and C were used for both the reactors since these do not vary significantly with changes in the feed composition. The lower value of k in the second reactor reflects that the feed to the second stage is more difficult to crack.

3.3.1 Model Solution

A step-by-step procedure for the solution of the model given by Eqns. (3.1) to (3.37) is given below:

1) Since the model equations are based on the true boiling points of the pseudo-components, the available ASTM (D1160) distillation data were converted into TBP curve following a procedure given in literature (Edmister, 1988; API Tech. Data Handbook, 1977). For the VGO feed used in this study, Table 3.2 gives the conversion of ASTM D1160 to the corresponding TBP data.

2) To obtain the feed composition in terms of pseudo-components, the TBP curve was divided into a number of sections at intervals of 25 K. This is shown in Figure 3.2. The feed to the first reactor consisted of eleven pseudo-components (boiling

TABLE 3.2 Conversion of D1160 to TBP

	ASTM 1160 1 atm		ASTM 1160 10mm Hg	TBP 10mm Hg	TBP 1 atm	TBP 1 atm
	K	°F	°F	°F	°F	K
IBP	593	608	350	312	562	568
10%	658	725	446	432	708	649
30%	688	779	495	489	773	685
50%	716	829.4	525	525	829.4	716
70%	741	874.4			874.4	741
100%	838	1049			1049	838
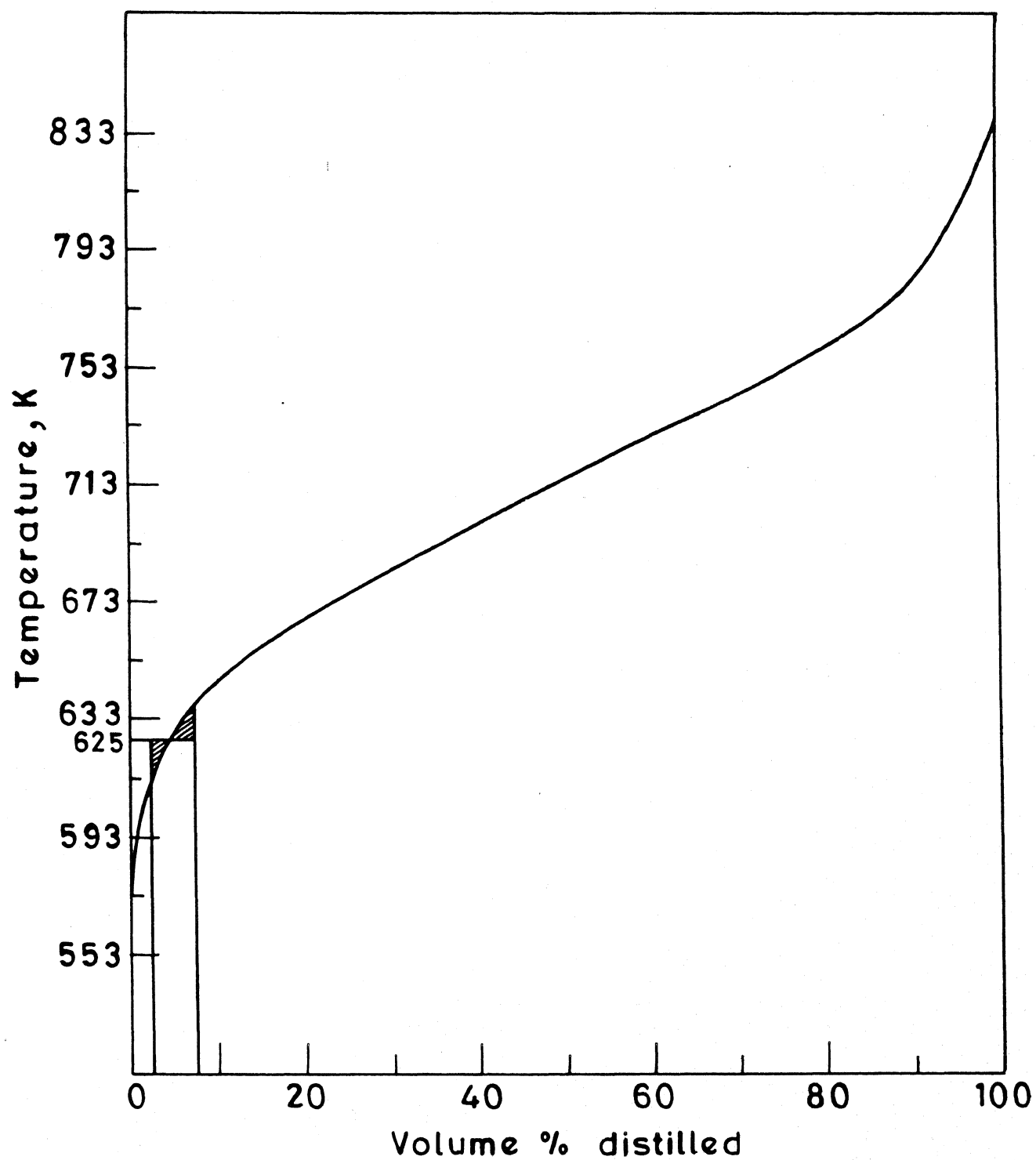
Fig.3.2 TBP curve for Vacuum Gas Oil.

range 563-838 K) whereas for the second reactor, the corresponding number was eight (boiling range 643-838 K). The pseudo-components were characterised by their specific ·gravity and average boiling point which was taken as the mid point of the 25 K interval (Figure 3.2). Specific gravities of the pseudo-components were estimated from available data for crude oils (Aalund, 1976). It has been assumed that the specific gravities for the pseudo-components in the VGO as well as hydrocracker product are the same as those available for the crude oil fractions of the same boiling range. Table 3.3 gives the characterisation of pseudo-components and the feed.

3) From the volumetric compositions, feed flow rate and specific gravity data (Tables 3.1 and 3.3), component mass flow rates and mass fractions were calculated.

4) Using Eqns. (3.4) through (3.6) the P_{ij}'s were calculated.

5) Using the P_{ij}'s and the carbon-to-hydrogen ratio (R_i') the stoichiometric hydrogen consumption as well as the heats of reaction were calculated by the procedure discussed in Section 3.2.5.

6) The specific rate constants were calculated by the method given in Section 3.2.3, using Eqns (3.9) and (3.10) and taking the reaction rate constant as given in Eqns. (3.38) and (3.39). Figure 3.3 shows the relative rate constants of the pseudo-components given by Eqn. (3.9).

7) Using Eqns (3.11) through (3.16), the molecular weight, T_c, P_c, V_c and ω were calculated (Table 3.4) and then using Eqns (3.19) through (3.27) the heat capacity of the liquid mixture as well as of individual pseudo-components were calculated. The sum of

TABLE 3.3 Characterisation of Pseudo-components and Feed

Comp no.	Boiling range K	Average boiling pt. K	$^{\circ}API$	Sp. gr. 288/288 K	Vol. %
1	263 - 288	275.5	110.8	0.58	-
2	288 - 313	300.5	99.7	0.61	-
3	313 - 338	325.5	81.8	0.66	-
4	338 - 363	350.5	68.4	0.71	-
5	363 - 388	375.5	60.1	0.74	-
6	388 - 413	400.5	54.7	0.76	-
7	413 - 438	425.5	49.1	0.78	-
8	438 - 463	450.5	46.6	0.79	-
9	463 - 488	475.5	44.7	0.80	-
10	488 - 513	500.5	41.5	0.82	-
11	513 - 538	525.5	38.4	0.83	-
12	538 - 563	550.5	35.2	0.85	-
13	563 - 588	575.5	33.5	0.86	1.5
14	588 - 613	600.5	32.5	0.86	3.0
15	613 - 638	625.5	30.2	0.88	4.0
16	638 - 663	650.5	28.6	0.88	9.5
17	663 - 688	675.5	26.1	0.90	14.5
18	688 - 713	700.5	24.8	0.91	15.5
19	713 - 738	725.5	22.4	0.92	18.5
20	738 - 763	750.5	20.5	0.93	14.0
21	763 - 788	775.5	19.2	0.94	11.0
22	788 - 813	800.5	17.6	0.95	5.2
23	813 - 838	825.5	15.6	0.96	3.3
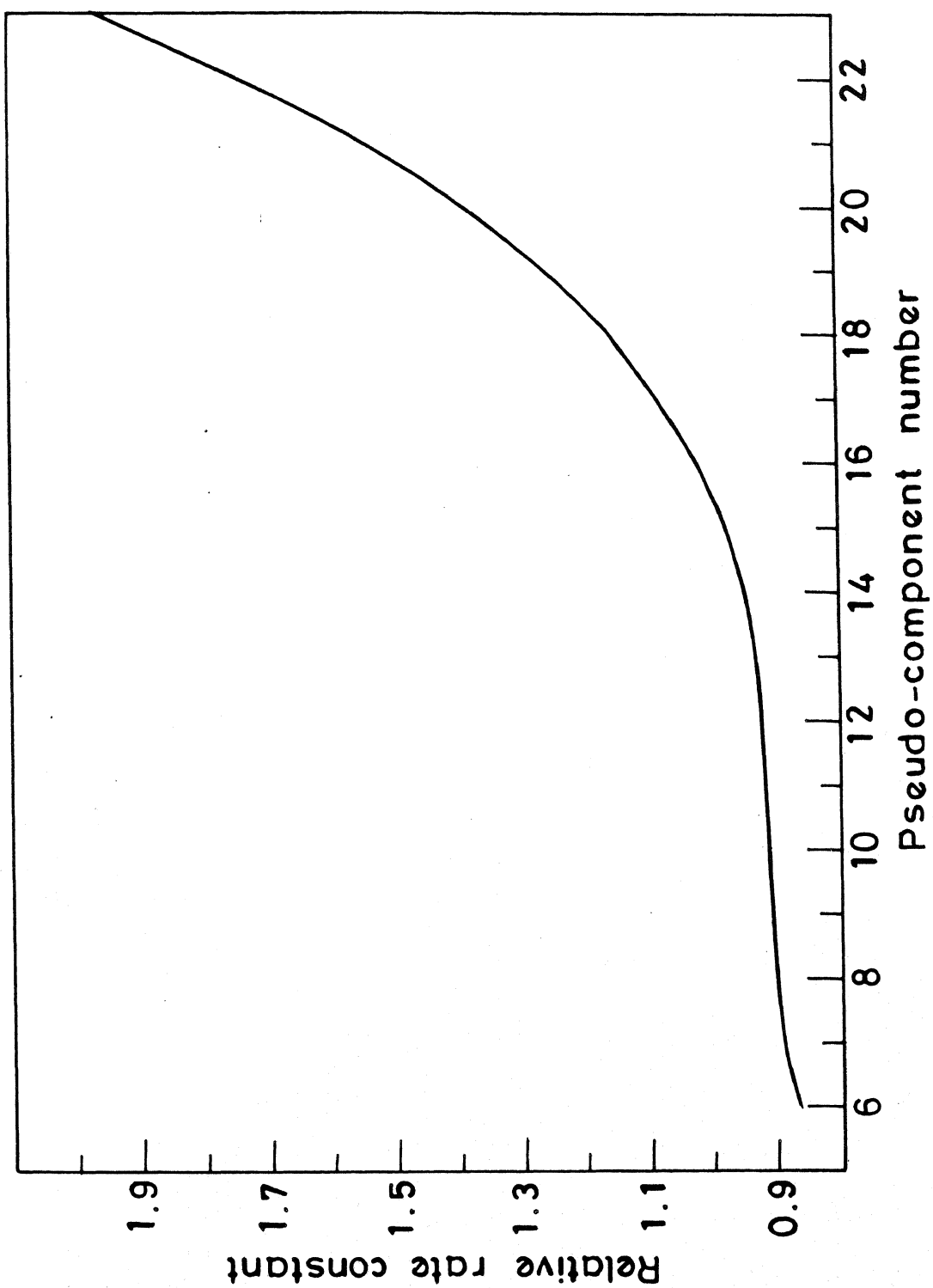
Fig. 3.3 Relative rate constant function.

TABLE 3.4 Estimated Properties of the Pseudo-components

Comp no.	UOPK	C/H	Mol. wt.	T_c,K	P_c, Atm.	ω
1	13.6	4.750	62	427.6	33.0	0.172
2	13.3	4.800	71	457.6	30.9	0.215
3	12.6	4.875	81	491.3	31.7	0.256
4	12.1	5.000	92	524.4	31.7	0.290
5	11.9	5.225	105	554.8	30.4	0.325
6	11.8	5.500	119	582.8	28.4	0.365
7	11.7	5.675	133	611.0	26.9	0.404
8	11.7	5.850	149	635.4	24.5	0.454
9	11.8	6.000	166	658.5	22.2	0.509
10	11.8	6.100	184	683.0	20.7	0.559
11	11.8	6.200	203	707.3	19.2	0.610
12	11.8	6.275	223	731.6	18.0	0.661
13	11.8	6.450	246	753.3	16.5	0.722
14	11.9	6.500	271	773.6	15.0	0.788
15	11.9	6.575	296	796.1	13.9	0.847
16	11.9	6.650	322	816.9	12.8	0.912
17	11.9	6.750	348	839.6	12.0	0.970
18	11.9	6.900	377	859.8	11.0	1.039
19	11.9	7.200	404	882.6	10.4	1.097
20	11.9	7.340	433	904.1	9.7	1.160
21	11.9	7.390	464	924.1	9.0	1.231
22	11.9	7.600	494	944.8	8.3	1.298
23	11.9	7.900	522	966.8	7.9	1.359

the product of the total liquid mass flow rate and heat capacity of the liquid mixture and the product of the mass flow rate of hydrogen and its heat capacity was used to calculate the term $\sum_i m_i Cp_i$ in Eqn (3.3).

8) Eqns. (3.2) and (3.3) were integrated numerically along the length of the catalyst bed in the first stage reactor using the Runge-Kutta-Gill method (Gill, 1951; Ralston and Wilf, 1965). The term $\sum_i m_i Cp_i$ was taken to be constant for each catalyst bed. The rate constants were evaluated at each integration step to account for the temperature effect.

9) The reaction mixture exiting from each catalyst bed was quenched by the recycle hydrogen. The total hydrogen flow rate to the next catalyst bed was then the initial hydrogen flow rate plus the hydrogen used for quenching. The inlet temperature of the reactants to the next bed was calculated by enthalpy balance.

10) Steps (8) and (9) were then repeated for all the beds in the first stage of the reactor . The total rate of hydrogen consumption in the first stage, HCON (kg/h), was calculated by subtracting the hydrogen content of the hydrocarbon products at the exit of the first reactor from the hydrogen content of the hydrocarbon feed at the inlet.

$$HCON = \sum_{i=1}^{23} [m_i/(R_i + 1)] - \sum_{j=r}^{23} [m_j/(R_j +1)] \qquad (3.40)$$

$$r = 13 \quad \text{first stage}$$

In Eqn. (3.40), m_i is the mass flow rate of pseudo-component i

at the exit of the reactor and m_j is the mass flow rate of pseudo-component j at the inlet of the reactor.

11) The effluent from the first reactor was fractionated and the fraction boiling above 643 K was fed to the second reactor. Assuming hundred percent efficiency of the fractionator, the pseudo-components 16 through 23 were present in the feed to the second stage. Since the boiling range of component 16 is from 638 to 663 K, only part of component 16 boiling above 643 K was included in the feed to the second stage. Assuming a linear distribution of the material boiling in this range, only 80% of component 16 was present in this stream.

12) The feed to the second stage consisted of heavy hydrocarbons recovered from the first stage (step 11) and a recycle stream from the second stage boiling above 643 K. The recycle stream was obtained by fractionating the effluent from the second stage in the same separator.

13) To start the calculations for the second stage, a knowledge of the flow rate and the composition of the recycle stream is necessary. Initially the composition and hence the specific gravity of the recycle stream was assumed to be the same as that of the heavy ends from the first stage. It was therefore possible to calculate the mass flow rate of the total feed to the second stage knowing the volumetric flow rate available from the plant. Since mass flow rate of stream from first stage was known, the recycle stream mass flow rate was obtained by difference.

14) Using the mass flow rates, the composition and the inlet temperature for the second reactor, steps (4) through (10) were

repeated. To obtain total hydrogen consumption in the second stage, Eqn. (3.40) is used with value of r=16.

15) The mass flow rate and composition of the recycle stream from the second stage were calculated as detailed in step (11) and compared with the assumed value (step 13). Successive substitution method was used to update the composition of the recycle stream until convergence was achieved within the pre-assigned tolerance limit.

16) Since no attempt has been made in the present study to model the fractionator, the product consists of the hydrocarbons boiling below 643 K formed in the two reactors. To compare the calculated yields with the plant data which were available only in four fractions namely high speed diesel (523-643 K), aviation turbine fuel (413-523 K), naphtha (288-413 K) and butanes and lighter fractions (<288 K), it was necessary to group the pseudo-components into corresponding boiling ranges as shown in Table 3.5

3.4 RESULTS AND DISCUSSION

A general program for the above model was written in Fortran-IV (Appendix - A) and was executed on DEC 1090 system. The CPU time required was two minutes six seconds.

The calculated yields, hydrogen consumption and exit temperatures are tabulated in Table 3.6 and have been compared with the plant data. Considering the uncertainties in evaluating the different model parameters, the calculated product yields are in good agreement with the plant data. It may be possible to tune the model parameters for a better match between the simulated results and plant data. However, due to the paucity of extensive

TABLE 3.5 Fraction of the Pseudo-component Present in the Products

Pseudo-components	HSD	ATF	Naphtha	Butanes and lighter fractions
1	–	–	–	1
2	–	–	1	–
3	–	–	1	–
4	–	–	1	–
5	–	–	1	–
6	–	–	1	–
7	–	1	–	–
8	–	1	–	–
9	–	1	–	–
10	–	1	–	–
11	3/5	2/5	–	–
12	1	–	–	–
13	1	–	–	–
14	1	–	–	–
15	1	–	–	–
16	1/5	–	–	–

HSD: high speed diesel

ATF: aviation turbine fuel

TABLE 3.6 Comparison of Calculated and Plant Data

	Calculated results	Plant data	% Error
Total feed to second stage (kg/h)	183236	183385	-0.08
Hydrogen consumption (kg/h)	1st 2816 2nd 1196	1st 3267 2nd 1363	-13.8 -12.2
Reactor outlet temperature (K)	1st 693.3 2nd 677.7	1st 714 (max) 2nd 700 (max)	— —
High speed diesel (wt.%)	48.79	50.5	-3.46
Aviation turbine fuel (wt.%)	30.53	29.4	+3.83
Naphtha (wt.%)	16.17	15.8	+2.51
Butanes and lower fractions	4.51	4.5	+0.22

experimental data, this was not attempted. The error in predicting the hydrogen consumption was significant, with the calculated values being lower than the plant values for both the stages. One possible reason for this discrepancy could be due to the fact that hydrodesulfurisation and hydrodenitrogenation reactions have not been included in this model. The sulfur content of the feed was 1.44 wt.%. If dibenzothiophene is taken as the representative sulfur compound in the feed, 4 moles of hydrogen would be required to hydrogenate one atom of sulfur. Thus, for desulfurisation, 730 kg of hydrogen would be required which amounts to approximately 16% of the total hydrogen consumption. The sulfur concentration at the exit of each reactor was not known, hence the chemical hydrogen consumption for the desulfurisation reactions could not be calculated. Another reason for the calculated values of the hydrogen consumption being lower, can be attributed to the method of calculating the C/H ratio of the pseudo-components as the actual hydrocarbon types present in a particular boiling range are not explicitly accounted for. As can be seen from Table 3.6, the calculated feed to the second stage reactor matches almost exactly with the experimental values, thus further validating the model. The calculated temperatures at the outlet of the first stage and second reactors are also shown in Table 3.6. Since the actual exit values of the temperatures were not available, these could not be compared but are within the specified maximum design limits.

For more extensive validation of the model, it is necessary to match the calculated temperature profiles along the reactors with the experimental profiles. Due to lack of plant data, this was not possible although the model does calculate the temperature profiles in each bed. Figure 3.4 shows the temperature
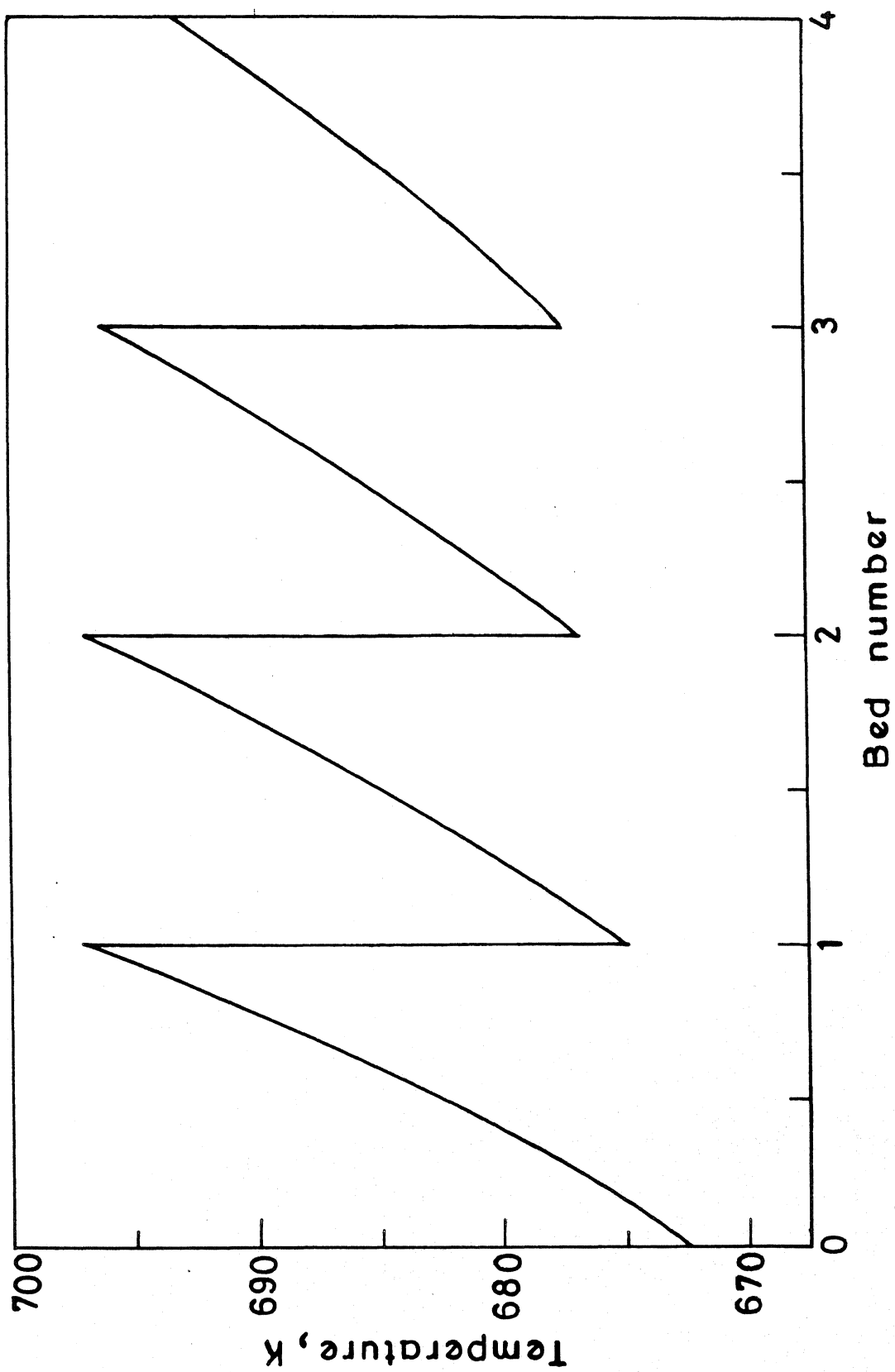
Fig.3.4 Temperature profile for the first stage.

profile along the length of the first reactor. The steep gradients are due to highly exothermic nature of the hydrocracking reactions. Since the reactor has been assumed to be adiabatic, the profiles for each bed are approximately parallel, with the temperature dropping due to hydrogen quenching between the catalyst beds. The temperature rise in successive catalyst beds decreases because the rate of hydrocracking is lowered as the average molecular weight of the reactants is reduced due to reaction.

The temperature profile in the second reactor (Figure 3.5) is significantly different from that of the first reactor. Due to reduced amount of the recycle hydrogen for quenching, the temperature drop between the beds in the second reactor is much less than that in the first stage. This leads to the outlet temperature from each bed rising progressively.

The variation of the concentration of some pseudo-components along reactor is shown in Figure 3.6 for both reactors. The pseudo-components chosen for depicting the concentration profiles are representative of the four products (viz. butanes, naphtha, ATF and HSD) and the feed. While the concentration of A_{20} (feed) monotonically decreases, those of the product increase. The net rate of formation of A_{14} (HSD) decreases continuously and is approximately zero in the last bed of the first reactor. In contrast, the concentration of this component continues to increase at an approximately constant rate throughout the second reactor. This may be attributed to the temperature profile in the two reactors. In both the reactors, the concentrations of the lighter components, A_1 (butanes and lighter fractions), A_4 (naphtha), and A_9 (ATF) continuously increase with
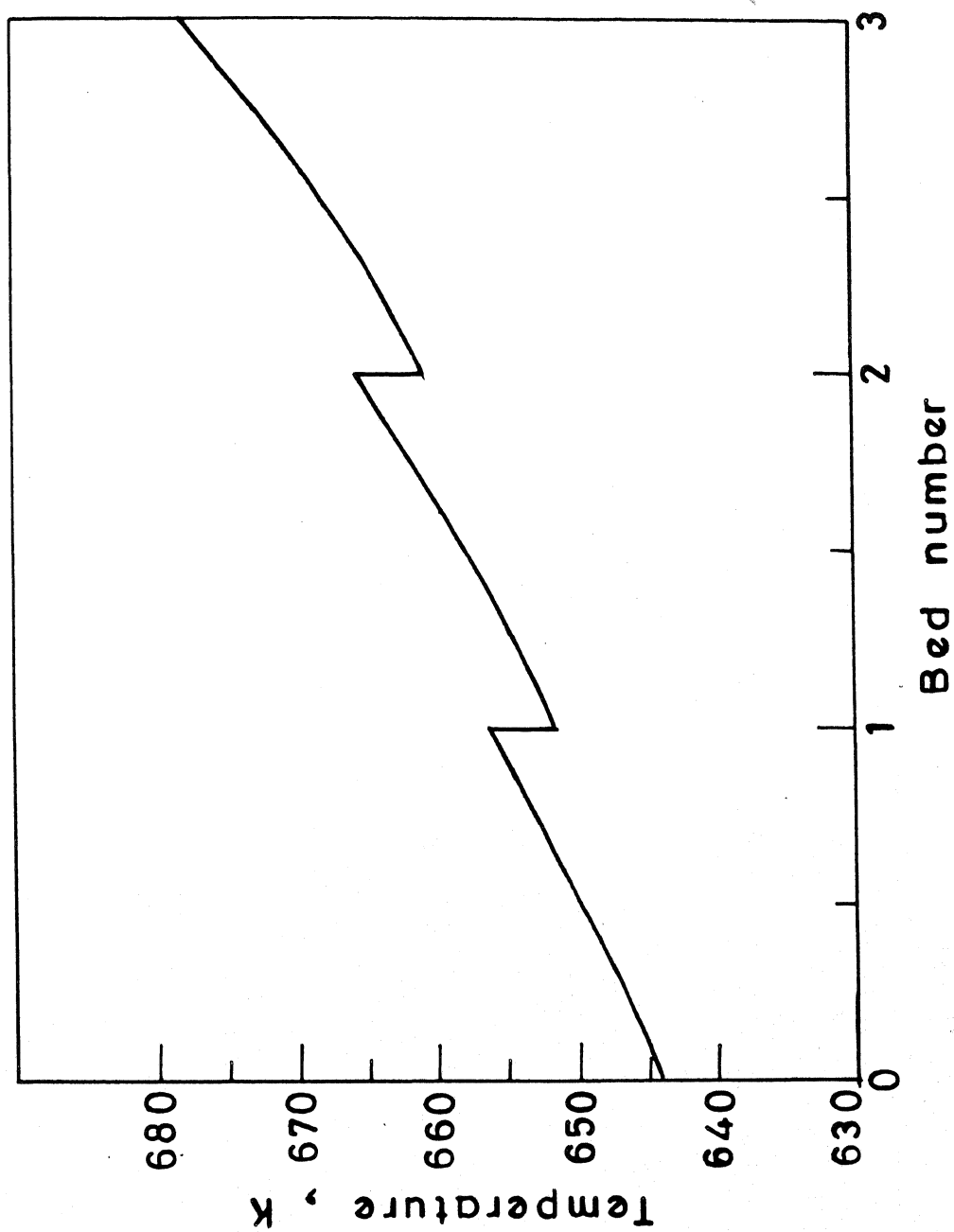
Fig. 3.5 Temperature profile for the second stage.
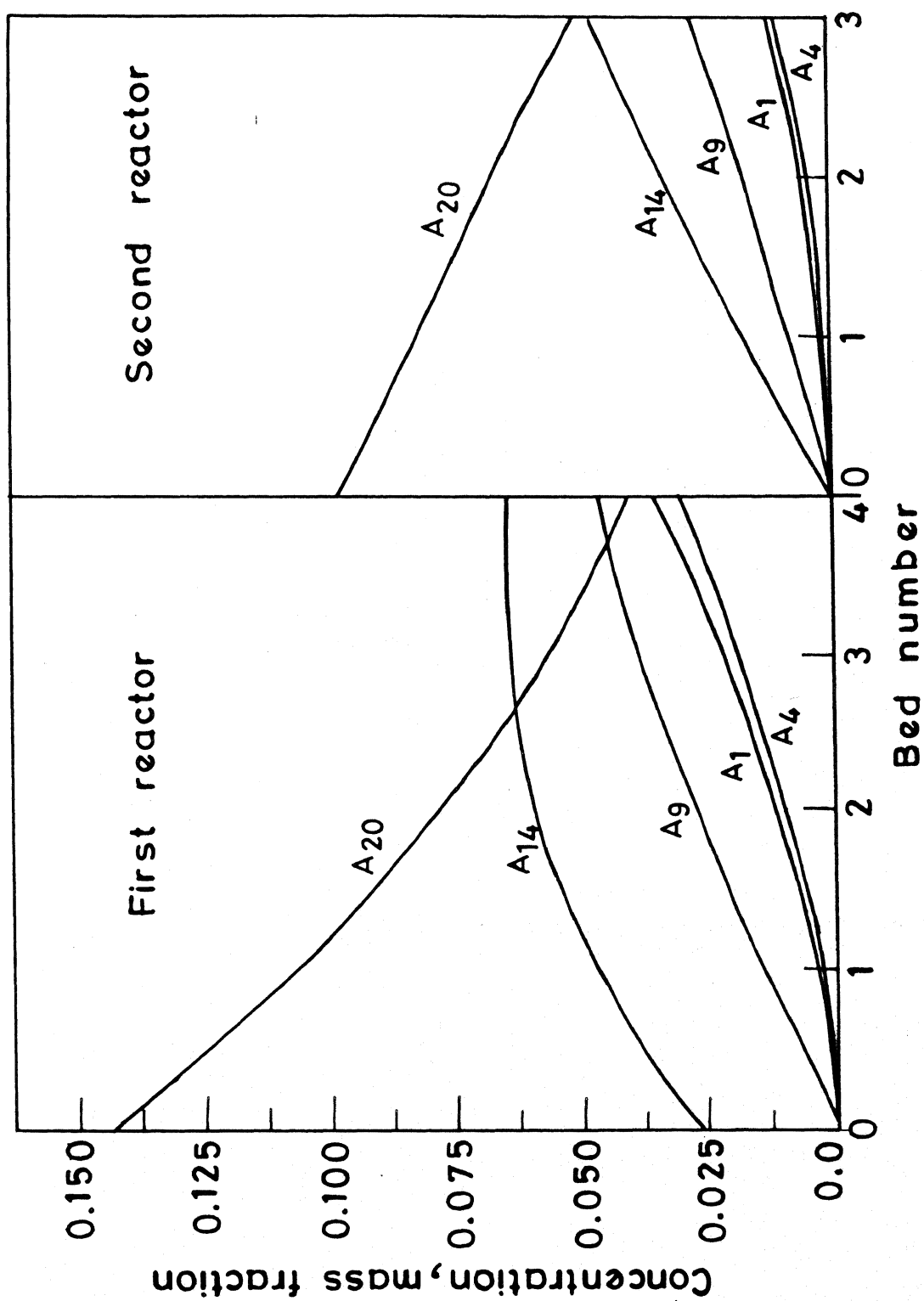
Fig.3.6 Concentration profiles of representative pseudo-components.

reactor length.

The product distribution at the end of each reactor is shown in Figure 3.7. Due to the lower bed temperatures in the second reactor, the extent of hydrocracking is less resulting in high concentration of the heavy components (components A_{16} - A_{23}) at the exit of the second reactor.

Sensitivity analysis was carried out to study the effect of various parameters on the reactor performance. In the present model, the parameters which affect the reactor performance are the parameters B and C and the operating conditions.

Effect of Model Parameters:

The parameter B is used for estimating the yield of pseudo-components 2 through 21 whereas the parameter C affects the yield of butanes and lighter fractions. With an increase in B, the yield of lighter fractions decreases whereas that of heavier fractions increases. Thus it would be expected that the recycle would increase with an increase in B. In the present model, an increase in B from 0.7 to 0.85 resulted in an increase of 7% in the recycle stream and 2.4% in high speed diesel at the exit of the first stage. However, there was a decrease of 7% in aviation turbine fuel, 17.4% in naphtha and 10.6% in butanes and lighter fractions for above change in B. An increase in the parameter C resulted in an increase in the yields of butanes and lighter fractions with negligible effect on the yield of other products. As C was increased from 0.37 to 0.47 the yield of butanes and lighter fractions increased from 3.5 to 4.5%.
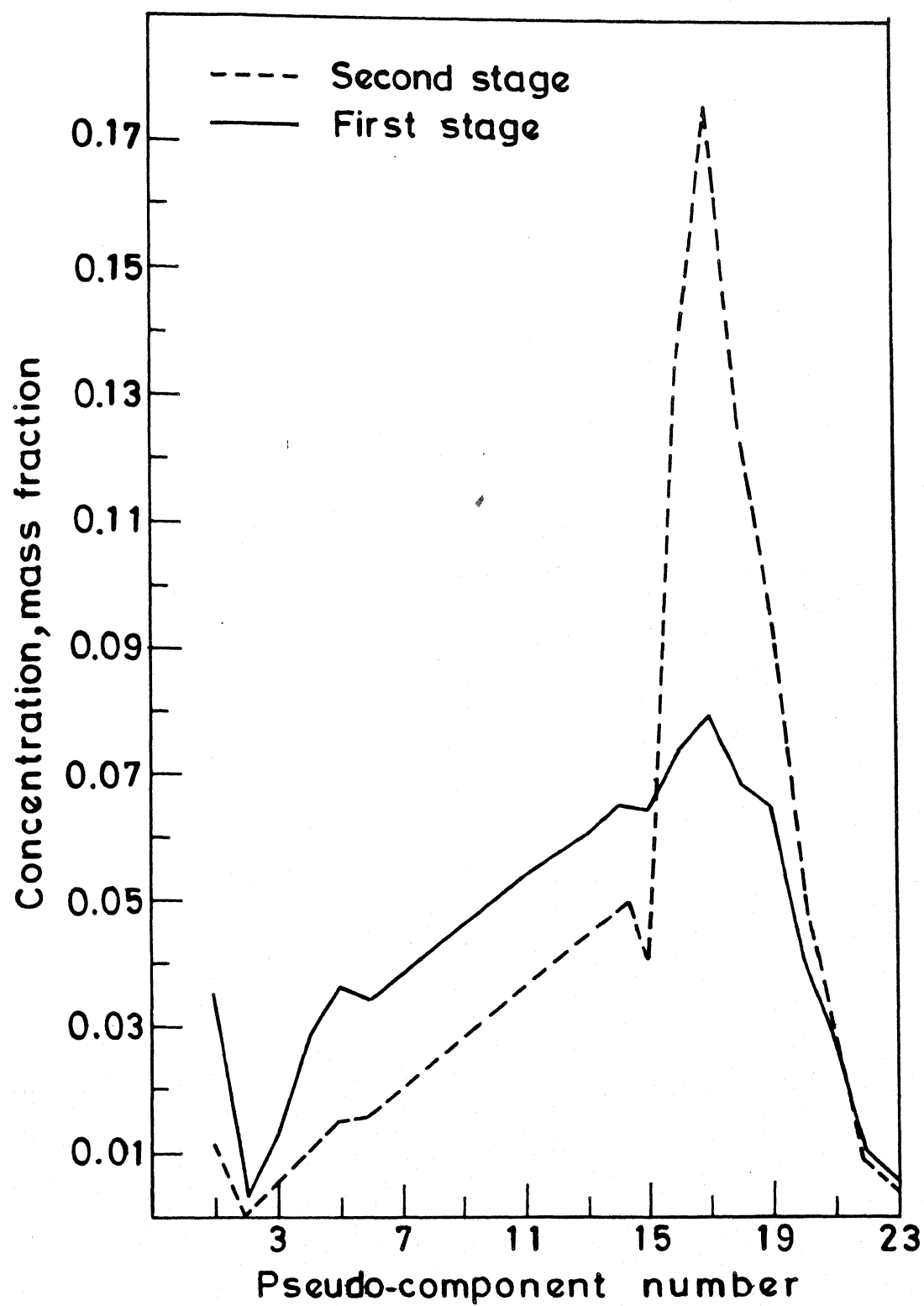
Fig.3.7 Product distribution at the exit
of the first and second stage.

Effect of Operating Conditions:

For any hydrocracker, temperature is the most important operating parameter. With an increase in the temperature, the rates of all the reactions would increase resulting in higher yields of lighter products. As the inlet temperature of the first reactor was increased from 672 K to 674 K the exit temperature increased from 693.3 K to 703.1 K. This indicates that the reactor is very sensitive to temperature variations which is in agreement with literature (Rapp and Van Driesen, 1969) where it is stated that very accurate control of temperature is required for a H-Oil hydrocracker. Possible reasons could include the highly exothermic nature of hydrocracking reactions coupled with the assumption of adiabatic operation. In addition to increasing the exit temperature by nearly 10 K, the two degree increase in the inlet temperature resulted in 11.6% decrease in recycle material, 7% increase in ATF, and 16% increase in naphtha. This temperature sensitivity requires that for steady state operation, the inlet temperature of the feed should be controlled accurately.

BIBLIOGRAPHY

Aalund, L.R. "Guide to World Crudes. 1" O & G J, 98-122, **74**(13), 1976.

API Technical Data Handbook- Petroleum Refining, 1977.

Archibald, R.C.; Greensfelder, B.S.; Holzman, G.; Rowe, D.H. "Catalytic Hydrocracking of Aliphatic Hydrocarbons" Ind. Eng. Chem., **52**, 745-750, 1960.

Coonradt, H.L.; Garwood, W.E. "Mechanism of Hydrocracking Reaction of Paraffins and Olefins" Ind. Eng. Chem. Process Des. Dev., **3**, 38-45, 1964.

Edmister, W.C., "Applied Hydrocarbon Thermodynamics" vol. 2, 2nd edition, Gulf Publishing Co., Houston, 1988.

El-Kady, F.Y.A. "Hydrocracking of Vacuum Distillate Fractions Over Bifunctional Molybdenum-nickel/Silica-alumina Catalyst", Ind. J. Tech., **17**, 176-183, 1979.

Flinn, R.A.; Larsen, O.A.; Beuther, H. "Mechanism of Catalytic Hydrocracking" Ind. Eng. Chem., **52**, 153-156, 1960.

Gary, W.W.; Rubin, L.C. "Total Heats of Gas Oils at Elevated Temperatures and Pressures" Ind. Eng. Chem., **25**, 178-183, 1933.

Gerdes, K.F.; Stangeland, B.E.; Chen, G.T.S.; Gumerman, R.J. "Simulation of Hydrocracking Reactor Systems", Paper presented at the Annual Meeting of AIChE, 1977.

Gill, S. "A Process for the Step-by-Step Integration of Differential Equations in an Automatic Digital Computing Machines" Proceedings of the Cambridge Philosophical Society, **47**, 96-108, 1951.

Goldfarb, Y.Y.; Katsobashvili, Y.R.; Rozental, A.L. "Study of Catalytic Hydrocracking of n-Decane, n-Undecane, n-Dodecane During

Long Catalysis Periods" Kinet. Katal., 22, 668-674, 1981.

Jaffe, B.E. "Hot Spot Simulation in Commercial Hydrogenation Processes" Ind. Eng. Chem. Process Des. Dev., 15(3), 410-416, 1976

Kesler, M.G.; Lee, B.I. "Improve Prediction of Enthalpy of Fractions" Hydrocarbon Processing, 55, 153-158, 55(3), 1976.

Krishna, R.; Saxena, A.K. "Use of an Axial-Dispersion Model for Kinetic Description of Hydrocracking" Chem. Eng. Sci., 44(3), 703-712, 1989.

Langlois, G.E.; Sullivan, R.F. "Chemistry of Hydrocracking" Reprinted from Adv. Chem. Ser., no. 9, 1970.

Lee, B.I.; Kesler, M.G. "A Generalised Thermodynamic Correlation Based on Three-Parameter Corresponding States" AIChE J., 21(3), 510-527, 1975.

Nelson, W.L. "Petroleum Refinery Engineering" 4th edition, Mc.Graw-Hill Book Co., Inc. New York, 169-171, 1958.

Peng, D.Y.; Robinson, D.B. "A New Two-Constant Equation of State" Ind. Eng. Chem. Fundam., 15, 59-64, 1976.

Perry, R.H.; Green, D.W. "Perry's Chemical Engineers' Handbook", 6th edition, Mc. Graw Hill Book Co., New York, 1984.

Qader, S.A.; Hill, G.R. "Hydrocracking of Gas Oils", Ind. Eng. Chem. Process Des. Dev., 8(1), 98-105, 1969.

Ralston, A.; Wilf, H.S. "Mathematical Methods for Digital Computers" Wiley, New York, 1965.

Rapaport, I.B. "Chemistry and Technology of Synthetic Liquid Fuels" 2nd ed., Israel Program for Scientific Translation, Ltd., Jerusalem, 1962.

Rapp, L.M.; Van Driesen, R.P. "H-Oil Process Gives Product Flexibility", Hydrcracking Handbook, Published by. Hydrocarbon Processing, Houston, Texas, Reprinted from Hydrocarbon Processing,

1969.

Reid, R.C.; Prausnitz, J.M.; Sherwood, T.K. "The Properties of Gases and Liquids" 3rd edition, Mc Graw Hill Book Co., 1977.

Satterfield, C.N. "Trickle Bed Reactors" AIChE J., 21(2), 209-228, 1975.

Scott, J.W.; Bridge, A.G. "Continuing Development of Hydrocracking" Advan. Chem. Ser., No. 103, 113-129,1971.

Smith, J.M.; Van Ness, H.C. "Introduction to Chemical Engineering Thermodynamics", McGraw Hill , New York, 1984

Stangeland, B.E. "A Kinetic Model for the Prediction of Hydrocracker Yields" Ind. Eng. Chem. Process Des. Dev., 13(1), 71-76, 1974.

Steijns, M.; Froment, G.; Jacobs, P.; Uytterhoeven, J. "Hydroisomerisation and Hydrocracking. 2. Product Distribution for n-Decane and n-Dodecane" Ind. Eng. Chem. Prod. Res. Dev., 20(4), 654-660, 1981.

Vansina, H.; Baltanos, M.A.; Froment, G.F. "Hydroisomerisation and Hydrocracking from n-Octane and 2,2,4-Trimethyl Pentane" Ind. Eng. Prod. Res. Dev., 22, 526-531, 1983.

Vargaftik, N.B. "Tables on the Thermophysical Properties of Liquids and Gases" Hemisphere Publishing Corporation, John Wiley and Sons, Inc., 1975.

Walas, S.H. "Phase Equilibria in Chemical Engineering" Butterworth Publishers, 1985.

Weir, H.M.; Eaton, G.L. "Heat Content of Petroleum - Oil Fractions at Elevated Temperatures" Ind. Eng. Chem., 24, 211-218, 1932.

Yu, W.C.; Lee, H.M.; Ligon, R.M. "Predict High Pressure Properties" Hy. Process., 171, Jan 1982.

CHAPTER - 4

MODELING OF HYDROTREATING REACTORS

4.1 INTRODUCTION

Hydrotreating of petroleum fractions is carried out to remove the sulfur, nitrogen, oxygen and heavy metal compounds as well as to stabilize the fractions by hydrogenation of the highly unsaturated compounds. Hydrogenation of sulfur compounds present in petroleum fractions commonly referred to as hydrodesulfurisation (HDS) has long been one of the major catalytic operations in the petroleum industry and forms an integral part of a modern oil refinery. Crudes containing high percentage of sulfur (eg. Middle East) have to be desulfurised to produce processible, stable, and environmentally acceptable liquid and lube base stocks.

The type of sulfur compound present in any fraction greatly depends on the boiling range of the fraction. The lower boiling fractions contain sulfur in the form of mercaptans and sulfides but as the boiling point range increases, more complex chemical form of sulfur compounds become predominant (Agarwal et al, 1973,1976). These complex sulfur compounds are generally in the form of thiophenes, benzothiophenes, dibenzothiophenes, naphthothiophenes, naphthobenzothiophenes, acenaphthenothiophenes etc. Low boiling fractions may also contain small amounts of hydrogen sulfide and elemental sulfur also. During HDS

ocracking and saturation of aromatics can also take place

.ltaneously. The hydrogen consumption increases rapidly as the

of the sulfur compound increases due to saturation and

cracking of large number of aromatic rings.

In the present study, models have been developed for HDS

reactors processing three different types of feedstocks: (i)

vacuum distillate (ii) kerosene and (iii) diesel. While the

reactor for vacuum distillate consisted of three catalyst beds,

the diesel and kerosene hydrodesulfurisers had a single catalyst

bed each (Figure 4.1). Some of the models published in literature

have been reviewed in Section 2.2.6.

4.2 CHEMISTRY

In the present models, all the sulfur compounds present

in the feed were represented by a single model sulfur compound.

Depending on the boiling range of the feed a different

representative model compound was chosen. The model compound

chosen for vacuum distillate was dibenzothiophene/ substituted

dibenzothiophene, for kerosene it was tri-substituted thiophene

(Paushkin, 1962) and for diesel, benzothiophene. The model sulfur

compounds for vacuum distillate and kerosene were selected such

that their boiling points were approximately at the middle of the

boiling range of the respective feeds. As suggested by Jewell et

al. (1976), benzothiophene was taken as the model compound for

diesel feed. It should be noted here that its boiling point

(494 K) is at the lower end of the boiling range of the feed

(493-688 K). Sulfur is removed in the form of hydrogen sulfide in

all the three cases. Dibenzothiophene requires 5 moles of hydrogen

per atom of sulfur if cyclohexylbenzene is formed and 2 moles of
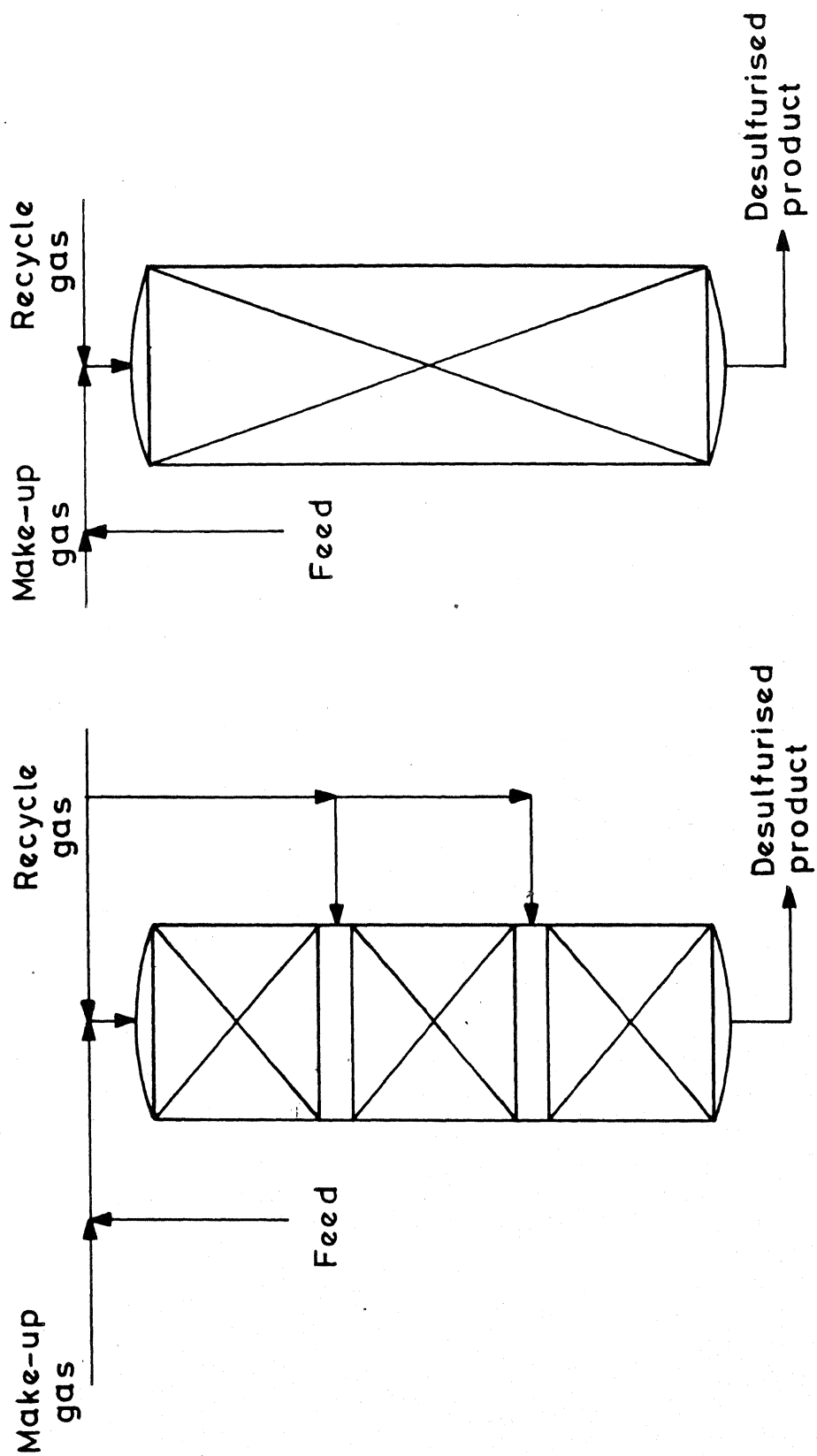
(a) Vacuum Distillate (b) Kerosene / Diesel

Fig. 4.1 Schematic diagram of the HDS reactors.

hydrogen if biphenyl is formed. Houlla et al. (1980) have shown that the substituted dibenzothiophenes also undergo similar reaction. Hoog (1950) reported that 35% of biphenyl and 65% of phenylcyclohexane plus bicyclohexyl is formed when dibenzothiophene is dissolved in tridecane solution and treated at 648 K and 50 atm.. The hydrogen consumption amounts to about 4 moles of hydrogen per mole of dibenzothiophene. The stoichiometric hydrogen required for HDS of tri-substituted thiophene is 4 moles per mole of sulfur compound and for benzothiophene it is 3 moles per mole of sulfur compound. The hydrogen consumption for the hydrocracking reaction will depend on the product distribution. Since the reaction conditions for HDS are less severe than those for hydrocracking, very little of cracking takes place. During HDS, hydrodenitrogenation, hydrodeoxygenation and hydrodemetallation reactions also take place but since the nitrogen, oxygen and metal content of the vacuum distillate feed considered in the present study were negligible (refer Table 4.1) and for the kerosene and diesel data were not available, these were not taken into account. The aromatics are generally present in considerable amounts in the lower boiling fractions. These may be in the form of naphthalene or its derivatives. In the present study aromatics were present in the kerosene fraction only (Table 4.2). Plant data revealed practically no saturation and hence it has not been accounted for. The characteristics of diesel oil are given in Table 4.3.

4.3 KINETICS

Several studies on the kinetics of pure sulfur compounds have been reviewed in Chapter 2. Although most of these studies

TABLE 4.1 Characteristics of Vacuum Distillate Feed

API gravity	22.0
Wt.% total sulfur	3.4
Metals, ppm max., Ni+V	0.3
Nitrogen, ppm	1000
TBP distillation (K)	
IBP	544.1
10%	618.0
30%	680.0
50%	704.1
70%	730.0
90%	763.0
100%	821.8

TABLE 4.2 Characteristics of Kerosene Feed

TBP cut point, K	430-558
API	43.5
TBP distillation, K	
IBP	388.6
10	430.2
30	467.7
50	494.1
70	517.7
90	553.8
100	588.6
Type analysis, LV%	
Paraffins	57
Naphthenes	21
Aromatics	22

TABLE 4.3 Characteristics of Diesel Feed

API	32
UOPK	11.8
Wt.% sulfur	2.0
TBP Distillation, K	
IBP	495.2
10%	548.0
30%	574.7
50%	598.0
70%	619.6
90%	644.7
100%	686.9

show that the reaction is first order with respect to the pure sulfur compound, for petroleum fractions, several authors have reported that the reaction is second order with respect to the total sulfur present in the feed (Chu and Wang, 1982; Papayannakos, 1986; Phillippopoulos and Papayannakos, 1988). They have stated that since in an industrial feedstock, a large number of sulfur compounds may be present, each of which will react at a rate proportional to its concentration, the overall order would be greater than one. Hence in the present study, second order kinetics has been assumed. For calculating the hydrogen consumption during hydrocracking, it was assumed that the vacuum distillate and the diesel feed could each be represented by a single component which cracks into two parts consuming one mole of hydrogen per mole of the component. Hydrocracking has been neglected for kerosene since this low molecular weight feed is not expected to crack significantly. First order kinetics has been assumed for the hydrocracking reaction (Qader and Hill, 1969; El-Kady, 1979).

4.4 MASS TRANSFER EFFECTS

The external mass transfer effects are negligible in commercial hydrodesulfurisers because of very high mass velocities (Schuits and Gates, 1973) but the internal mass transfer resistances which exist within the catalyst pores may be important for various type of feedstocks ranging from distillate to residue. The rate of transfer of hydrogen or sulfur containing oil molecules may be much slower compared to the intrinsic reaction rate and to account for this, the intrinsic rate has to be multiplied by the effectiveness factor. With an increase in pore

diameter, the effectiveness factor increases. Schuit and Gates (1973) have reported that an effectiveness factor of slightly less than one is applicable to many types of feeds and catalysts. Philippopoulos and Papayannakos (1988) have shown that the effectiveness factor for crushed HT-400E catalyst particles is greater than 0.75. In the absence of detailed intrinsic kinetics and catalyst specifications, it was not possible to calculate the effectiveness factor and hence in all the three cases it was assumed to be unity.

4.5 THERMODYNAMIC PROPERTIES ESTIMATION

The various properties such as the critical pressure, critical volume and enthalpy were estimated using the Lee-Kesler's method (Lee and Kesler, 1975; Kesler and Lee, 1976) and the enthalpies estimated from the excess enthalpies calculated based on Peng-Robinson's EOS (See Section 3.2.4 for details). Although the vacuum distillate feed was in the liquid phase and the kerosene in the vapour phase, the feed to the diesel hydrodesulfuriser was in a partially vapourised state. Hence, vapour-liquid equilibrium (VLE) constants are required for estimating the vapour and liquid compositions at any position along the reactor. The cubic EOS such as the Soave (1972) and Peng Robinson (1976) are generally used for predicting the vapour-liquid equilibrium constants of hydrocarbon mixtures. The distribution coefficient (K_i) for any component i, in a nonideal mixture is given as (Walas,1985);

$$K_i = \frac{\hat{\emptyset}_{iL}}{\hat{\emptyset}_{iV}} \qquad (4.1)$$

where $\hat{\varnothing}_{iL}$ and $\hat{\varnothing}_{iV}$ are the partial fugacity coefficients of the ith component in the liquid and vapour phases, respectively. However, due to lack of suitable correlation for evaluation of K_i for hydrocarbon mixture containing hydrogen, ideal K values were used. Lee Kesler's modification of Pitzer equation (Reid et al., 1977) was used for predicting the vapour pressure as given below. The reduced vapour pressure for any pseudo-component was estimated from

$$\ln Pvp_{ri} = f_i^{(o)}(T_{ri}) + \omega_i f_i^{(1)}(T_{ri})$$ (4.2)

where $f_i^{(o)} = 5.92714 - \dfrac{6.09648}{T_{ri}} - 1.28862 \ln T_{ri} + 0.169347 \, T_{ri}^6$

$f_i^{(1)} = 15.2518 - \dfrac{15.6875}{T_{ri}} - 13.4721 \ln T_{ri} + 0.43577 \, T_{ri}^6$

Pvp_{ri} is the reduced vapour pressure of component i and T_{ri} is the reduced temperature of component i. The vapour pressure (Pvp_i) can then be calculated from

$$Pvp_i = P_{ci} \cdot Pvp_{ri}$$ (4.3)

and $$K_i = \dfrac{Pvp_i}{P_T}$$ (4.4)

where P_{ci} is the critical pressure, in atms., of component i and P_T is the total pressure (atm).

The following expressions were used for calculating the mixture critical properties for the hydrogen gas mixture (Reid et

al., 1977).

$$T_{cm} = \sum_{j=1}^{N1} \varphi_j \; T_{cj} \qquad (4.5)$$

where N1 is the total number of components in the gas mixture

and

$$\varphi_j = \frac{y_j \; V_{cj}}{\displaystyle\sum_{i=1}^{N1} y_i \; V_{ci}} \; .$$

y_i and y_j are the mole fractions of the components i and j respectively, V_{ci} and V_{cj} are the critical volumes of components i and j respectively, T_{cj} is the critical temperature of component j and T_{cm} is the critical mixture temperature.

$$V_{cm} = \sum \Theta_j \; V_{cj} + \sum_{i=1}^{N1} \sum_{j=1}^{N1} \Theta_i \Theta_j \; \gamma_{ij} \qquad (4.6)$$

where

$$\Theta_j = \frac{y_j \; V_{cj}^{2/3}}{\sum y_i \; V_{ci}^{2/3}} \; ,$$

$$\gamma_{ij} = \psi_v \left(\frac{V_{ci} + V_{cj}}{2} \right) \; ,$$

$$\psi_v = A + B \; \delta_v + C \; \delta_v^2 + D \; \delta_v^3 + E \; \delta_v^4 \; ,$$

and

$$\delta_v = \frac{V_{ci}^{2/3} + V_{cj}^{2/3}}{V_{ci}^{2/3} + V_{cj}^{2/3}} \; .$$

θ_j is the surface fraction for component j, γ_{ij} is the binary interaction parameter for components i and j and V_{cm} is the mixture critical volume. Eqn. (4.6) is valid only for values of δ_v between zero and 0.5.

For binary systems containing hydrogen sulfide,

$A = -0.4957$; $B = 17.1185$; $C = -168.56$; $D = 587.05$; $E = -698.89$ and for all other binary systems in this model,

$A = 0.1397$; $B = -2.9672$; $C = 1.8337$; $D = -1.536$; $E = 0$.

4.6 HEATS OF REACTION

Although the theory for computation of heat of reaction is well understood, accurate estimation for petroleum fractions is seldom possible because of lack of adequate data such as precise stoichiometry, physical properties and heats of combustion. Since there are a large number of sulfur compounds present in the feed and their composition is not known, the use of heat of combustion data for calculating the heat of reaction is not possible. In this model, the heat of reaction has been calculated based on hydrogen consumption. Hydrodesulfurisation is an exothermic reaction and heat released during the reaction is of the order of 50 to 90 MJ/kmol of hydrogen consumed (Schuits and Gates, 1973). The heat released during HDS reaction at the reaction temperature and pressure as supplied by the plant is 62 MJ/kmol of hydrogen consumed for hydrodesulfurisation of vacuum distillate, diesel and kerosene feedstocks. In the present model, plant values have been used for calculating heat of reaction for HDS. Thus the heat of reaction for the HDS reaction is given by

$$(\Delta H_R)_s = - \frac{62 \text{ (no. of moles of } H_2 \text{ required / atom of S)}}{\text{(molecular weight of S)}}$$

$$(4.7)$$

$$\text{or} \quad (\Delta H_R)'_s = 32 \, (\Delta H_R)_s \tag{4.8}$$

where $(\Delta H_R)_s$ is in MJ / kg sulfur reacted and $(\Delta H_R)'_s$ is in MJ / kmol sulfur reacted.

The heat of reaction for the hydrocracking reaction was obtained as follows using the same value as in Chapter 3.

$$(\Delta H_R)_c = - \frac{42 \text{ (no.ofmoles of } H_2 \text{ required per mole of feed)}}{\text{(average molecular weight of the feed)}}$$

$$(4.9)$$

$$(\Delta H_R)'_c = (\Delta H_R)_c \text{ (average molecular weight of feed)} \tag{4.10}$$

where $(\Delta H_R)_c$ is in MJ / kg feed cracked and $(\Delta H_R)'_c$ is in MJ / kmol feed cracked.

4.7 MODEL ASSUMPTIONS

The assumptions made in this model were similar to those made for the modeling of hydrocracking reactor. The assumptions are:

    (i)   plug flow behaviour

    (ii) steady state conditions

   (iii) adiabatic operation

   (iv) negligible external mass transfer resistances

    (v) negligible pore diffusion resistance

   (vi) only HDS and hydrocracking reactions important

In this model, all the sulfur compounds have been

represented by a single compound following second order kinetics. Because of excess hydrogen present, the rate of HDS has been assumed to be independent of hydrogen partial pressure. Since the extent of hydrocracking was not significant, the entire feed has been represented by a single pseudo-component following first order kinetics for estimating the extent of hydrocracking.

4.8 MODEL DEVELOPMENT

The model for each HDS reactor consists of a set of differential mass balance and energy balance equations and a number of algebraic equations which are used for estimating the thermodynamic properties of the different fractions of the feed. For calculating the enthalpy of the mixture, the feeds were divided into N pseudo-components. A 20 K interval was used for vacuum distillate and kerosene whereas, diesel was divided at 15 K intervals. The enthalpy calculation procedure was the same as discussed in Section 3.2.4.

4.8.1 Vacuum Distillate Feed

Material Balance Equations :

The differential form of the mass balance equation based on the above assumptions can be written as

$$M_t(dC_s/dW) = -k_s C_s^2 \qquad (4.11)$$

where, C_s is the mass fraction of sulfur, M_t is the total mass flow rate and k_s is the second order rate constant.

The differential mass balance equation to account for the hydrocracking reaction can be written as,

$$M_t(dC_c/dW) = -k_c C_c \qquad (4.12)$$

where C_c is the mass fraction of the feed to be cracked, and k_c is the first order rate constant.

Energy Balance Equation :

The differential form of the heat balance equation for an adiabatic reactor can be written as

$$dT/dW = \frac{1}{\sum_i m_i Cp_i} [(-\Delta H_R)_s k_s C_s^2 + (-\Delta H_R)_c k_c C_c] \qquad (4.13)$$

$$i=1, \ldots\ldots\ldots N+1$$

where T is the reactor temperature. The (N+1)th component is the gas phase. The summation of the product of the component mass flow rate and its heat capacity is assumed to be constant for each catalyst bed.

4.8.2 Kerosene Feed

In contrast to the HDS of vacuum distillate where the feed was in the liquid phase, the kerosene feed was in a completely vapourised state. Thus, it was more convenient to express the total feed on a molar basis and the concentrations in partial pressures. Using compressibility factor, Z, to represent the nonideal behaviour, the concentration of any component i, C_i, can be expressed in terms of its partial pressure, P_i, as

$$C_i = \frac{P_i}{Z R T} = \frac{P_T y_i}{Z R T} \qquad (4.14)$$

where y_i' is the mole fraction of component i. Hydrocracking reactions are not very significant in case of kerosene hydrodesulfurisation because of mild operating conditions and hence have not been included.

Mole balance equation

The differential mole balance equation for the HDS reaction can be writen as

$$\frac{F_t P_T}{Z R T} \frac{dy_s'}{dW} = - k_s \frac{P_T^2 \, y_s'^2}{Z R T} \tag{4.15}$$

where F_t is the total volumetric flow rate, y_s' is the mole fraction of sulfur compound and k_s is the second order rate constant. F_t can also be written as

$$F_t = \frac{Z N_t R T}{P_T} \tag{4.16}$$

where N_t is the total molar flow rate. Substituting Eqn (4.16) into Eqn. (4.15), one obtains

$$\frac{dy_s'}{dW} = - \frac{k_s P_T^2 \, y_s'^2}{N_t Z^2 R^2 T^2} \tag{4.17}$$

Energy balance equation

The differential form of the energy balance equation in terms of partial pressures can be written as

$$\frac{dT}{dW} = \frac{1}{\sum\limits_i n_i Cp_i} (- \Delta H_R)_s' \, k_s \left(\frac{P_T \, y_s'}{Z R T}\right)^2 \tag{4.18}$$

$$i = 1,.....(N+1)$$

where n_i is the molar flow rate of component i and Cp_i is the molar heat capacity. (N+1)th component is the hydrogen gas mixture.

4.8.3 Diesel Feed

While kerosene was completely in the vapour phase and vacuum distillate in the liquid phase, the diesel was a partially vapourised feed. The model proposed for diesel hydrodesulfuriser takes into account the vapour-liquid equilibria, in addition to the material and energy balance equations. For treating a feed which is in partially vapourised state, it is necessary to have a reliable estimate of vapour-liquid equilibrium constants for the different components in the mixture. Using Eqns. (4.2) through (4.4) and the critical properties, the ideal vapour-liquid equilibrium ratio for benzothiophene was calculated to be approximately 0.26 at 613 K. As mentioned earlier, the boiling point of benzothiophene is at the lower end of the boiling range of diesel, the sulfur compounds present would have a lower K-value and, therefore the sulfur compounds were to be in the liquid phase only.

Mole balance equations

With the above assumption, the differential form of sulfur mole balance equation can be written as

$$N_{tl} \frac{dx_s}{dW} = - k_s x_s^2 \tag{4.19}$$

where N_{tl} is the liquid molar flow rate and x_s is the molar concentration of sulfur in the liquid phase. Similarly , the mass balance equation for the hydrocracking reaction can be written as

$$N_{tl} \frac{dx_c}{dW} = - k_c \, x_c \qquad (4.20)$$

where x_c is the mole fraction of the uncracked feed in the liquid phase.

Energy balance equation

The differential energy balance can be written as

$$\frac{dT}{dW} = \frac{1}{(N_{tl} \sum_i x_i Cp_i + N_{tv} \sum_i y_i Cp_i)} [(-\Delta H_R)_s \, k_s \, x_s^2 + (-\Delta H_R)_c \, k_c \, x_c]$$

$$i = 1,2...(N+1)$$

$$(4.21)$$

where x_i and y_i are the mole fractions of component i in the liquid and vapour phases, respectively.

Vapour – Liquid Equilibria

The following equations are used to estimate the vapour and liquid compositions along the length of the reactor..

Overall mole balance : $N_t = N_{tl} + N_{tv}$ (4.22)

Component mole balance : $N_t \, z_i = N_{tl} \, x_i + N_{tv} \, y_i$ (4.23)

$$\sum z_i = \sum x_i = \sum y_i = 1 \qquad (4.24)$$

By re-arranging Eqns (4.22), (4.23), (4.24), we have

$$\Sigma \frac{z_i}{[1 + \frac{N_{tv}}{N_t}(K_i - 1)]} = 1 \tag{4.25}$$

and

$$x_i = \frac{z_i}{[1 + \frac{N_{tv}}{N_t}(K_i - 1)]} \tag{4.26}$$

where N_t is the molar flow rate of the reactant mixture to be flashed and z_i is the mole fraction of the ith component in the reaction mixture.

4.9 HYDROGEN CONSUMPTION

Knowing the extent of hydrodesulfurisation and hydrocracking the rate of hydrogen consumption in kg/h, HCON, could be calculated.

(i) Vacuum Distillate HDS:

$$HCON = 2.0\ M_t [\frac{(C_s^i - C_s^o)(\text{no. moles of } H_2 \text{ consumed / atom of S})}{(\text{molecular weight of S})}$$

$$+ \frac{(C_c^i - C_c^o)(\text{no. of moles of } H_2 \text{ consumed / mol of feed})}{(\text{average molecular weight of the feed})}]$$

$$\tag{4.27}$$

where C_s^i and C_s^o are the mass fraction of sulfur at the inlet and exit of the reactor, respectively. C_c^i and C_c^o are the mass fraction of uncracked feed at the inlet and outlet of the reactor, respectively.

(ii) Kerosene HDS

$$\text{HCON} = 2.0 \ (N_t^i {y_s'}^i - N_t^o {y_s'}^o)(\text{no. of moles of } H_2 \text{ consumed / atom of S})$$

$$(4.28)$$

where N_t^i and N_t^o are the molar flow rate at the inlet and exit of the reactor, respectively; ${y_s'}^i$ and ${y_s'}^o$ are the mole fractions of sulfur at the inlet and exit of the reactor, respectively.

(iii) Diesel HDS:

$$\text{HCON} = 2 \ [(N_{tl}^i {x_s'}^i - N_{tl}^o {x_s'}^o)(\text{no. of moles of } H_2 \text{ consumed/atom S})$$

$$+(N_{tl}^i {x_c'}^i - N_{tl}^o {x_c'}^o)(\text{no. of moles of } H_2 \text{ consumed /mol feed})]$$

$$(4.29)$$

where ${x_c'}^i$ and ${x_c'}^o$ are the mole fractions of the uncracked feed at the inlet and outlet of the reactor, respectively. N_{tl}^i and N_{tl}^o are the liquid molar flow rate at the inlet and exit of the reactor, respectively.

4.10 APPLICATION OF THE MODELS

The above models were used for the simulation of a single or multi-bed reactors. The feeds were obtained from processing of a mixture of various crudes such as Arab light, Arab Heavy and Murtan. The content and distribution of sulfur compounds in these crudes do not vary significantly. The TBP as well as the sulfur, nitrogen and metal concentrations of the vacuum distillate, kerosene and diesel feeds are tabulated in Tables 4.1, 4.2 and 4.3 respectively. The TBP cuves for these feeds are shown

in Figure 4.2 and the specifications of the catalyst used is given in Table 4.4. The plant data for the vacuum distillate HDS is given in Table 4.5.

4.10.1 Vacuum Distillate:

The boiling range of the vacuum distillate feed was 544-822 K. The representative sulfur compound chosen for vacuum distillate feed was dibenzothiophene (b.p. 605 K) / substituted dibenzothiophene . Phillippopoulos and Papayannakos (1988) have reported a second order rate constant for hydrodesulfurisation of non-asphaltenic sulfur present in crude oil residue (boiling point > 315 °C) on the same type of catalyst for which plant data were available (HT-400E), as

$$k_s = 3.78 \times 10^{11} e^{-13500/T} \frac{(kg\ feed)^2}{(kg\ cat.)(kg\ S)(h)} \qquad (4.30)$$

since no rate constants are available in the published literature for vacuum distillate HDS, the above value of k_s was used as a first estimate and was later adjusted to a final value of

$$k_s = 2.92 \times 10^{11} e^{-13500/T} \frac{(kg\ feed)^2}{(kg\ cat.)(kg\ S)(h)} \qquad (4.31)$$

to obtain a better match between the model predictions and the plant data.

El-Kady (1979) reported hydrocracking rate constant for vacuum distillate but on a different catalyst as

$$k_c = 0.2420 \times 10^9 e^{-13416/T} \frac{kg\ feed}{(kg\ cat.)(h)} \qquad . \qquad (4.32)$$
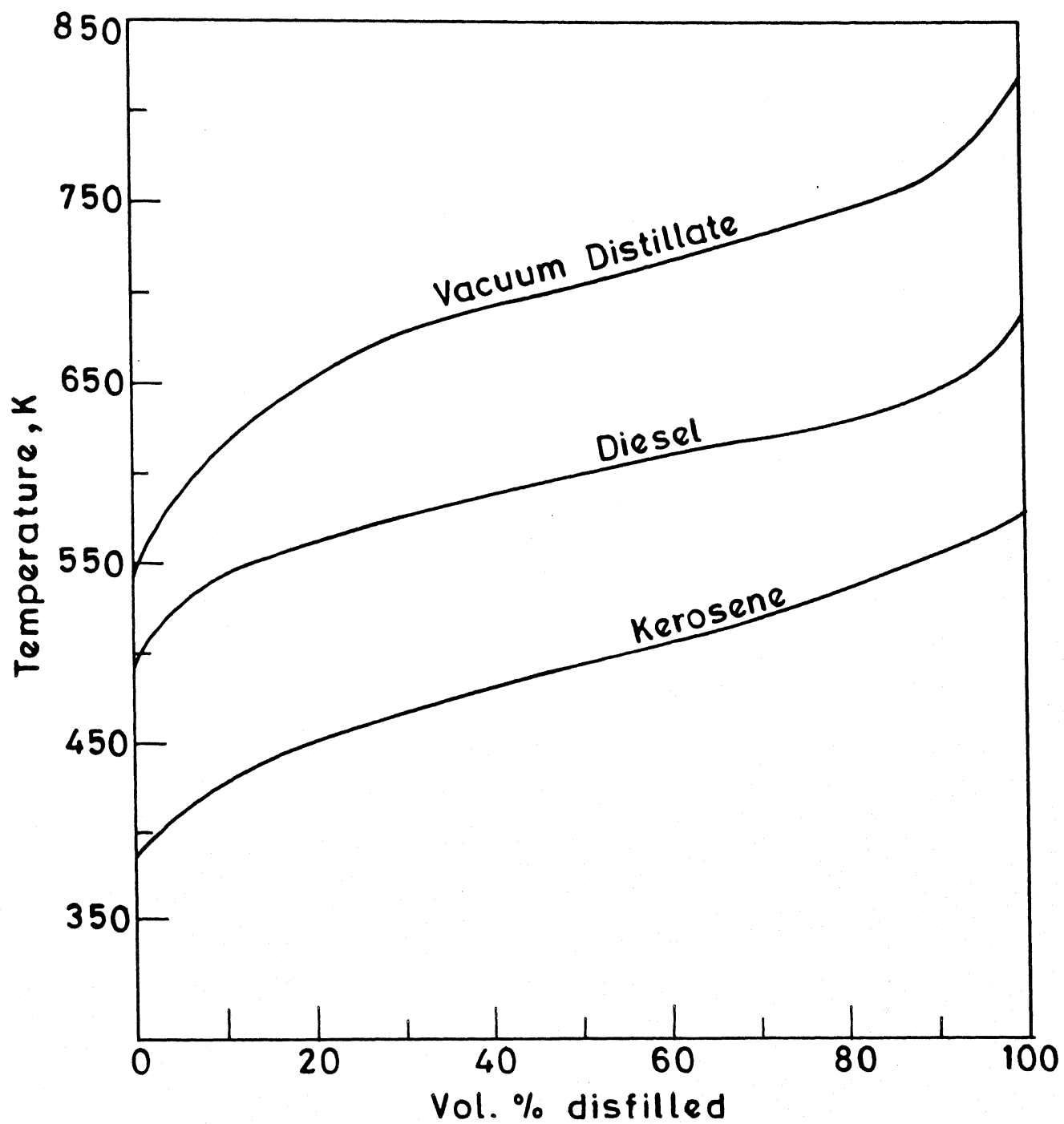
Fig. 4.2   TBP curves for HDS feeds.

TABLE 4.4 Catalyst Specifications

Type	HT-400E
Size (extrudates), inch	1/6
Bulk density, kg/m^3	725
Metal content (calcined basis), %	
CoO	3
MoO_3	15
Surface area, m^2/kg	22×10^4
Cum-Pore volume, m^3/kg	500
Average crush strength, kg	26.4

TABLE 4.5 Plant Data for Vacuum Distillate Unit

Flow rate of vacuum distillate, m^3/h	43.7
Reactor inlet temperature, K	631
Average reactor pressure, atm	63
Recycle gas, Nm^3/h	7240
Purity of recycle gas, vol.%	78
Make-up gas, Nm^3/h	4000
Purity of make-up gas, vol.%	95
Reactor quench at the exit of 1st and 2nd bed, Nm^3/h	6630
Sulfur in feed, wt.%	3.4
Number of catalyst beds	3
Catalyst volume in each bed	11.67

In the absence of information on kinetics of hydrocracking on the present catalyst, El-Kady's rate constant was used with a modified pre-exponential factor of 4.11 x 10^7 to minimize the discrepancy between predicted and measured values.

For solving the energy balance equation (Eqn. 4.13), the heat capacities of the pseudo-components in the liquid phase and of the hydrogen gas mixture are required. The liquid heat capacities were obtained as discussed in Section 3.2.4. The make-up and recycle hydrogen were not 100 % hydrogen.In addition to hydrogen, the gas mixture consisted of several hydrocarbons, the predominant constituent being methane. The heat capacity of the gas mixture was, therefore, calculated assuming that only hydrogen and methane were present. The heat capacity of hydrogen was taken to be 14.5 kJ/(kmol)(K) and that for methane as 3.46 kJ/(kmol)(K) (Vargaftik, 1975).

A step by step procedure for the solution of the model equations is given below.

1) From the given TBP data (Table 4.1), the TBP curve shown in Figure 4.2 was plotted. The TBP curve was divided into smaller sections of 20 K interval to obtain the feed composition in terms of pseudo-components. Each pseudo-component was characterised by its specific gravity and average boiling point which was taken as the mid-point of the 20 K interval. The specific gravity data for the pseudo-components were obtained from the plant. Table 4.6 gives the characterisation of the pseudo-components.

TABLE 4.6 Characterisation of Pseudo-components in Vacuum
Distillate

Comp. no.	boiling range, K	mid boiling pt., K	Sp. Gr.	UOP K	Vol.%
1	543-563	553	0.838	11.9	2.0
2	563-583	573	0.848	11.9	2.0
3	583-603	593	0.856	11.9	3.2
4	603-623	613	0.864	12.0	4.2
5	623-643	633	0.874	12.0	5.0
6	643-663	653	0.882	12.0	6.0
7	663-683	673	0.890	12.0	7.5
8	683-703	693	0.90	12.0	18.5
9	703-723	713	0.910	12.0	16.5
10	723-743	733	0.920	11.9	15.0
11	743-763	753	0.930	11.9	10.0
12	763-783	773	0.944	11.8	4.3
13	783-803	793	0.956	11.8	3.3
14	803-823	813	0.968	11.7	2.5

2) From the volumetric composition, feed flow rate and specific gravity, the component mass flow rates and mass fractions were calculated.

3) From the volumetric flow rate and purity of the gas and specific gravity data; mass flow rate of the gas at the inlet of the reactor was calculated.

4) Using Eqns (3.11) through (3.16), the molecular weight, T_c, P_c, V_c and ω of the pseudo-components were calculated (Table 4.7). Using Eqns. (3.19) through (3.27a), the heat capacity of the liquid mixture was calculated. Knowing the heat capacities and mass flow rates for liquid and gas phases, the term $\sum_i m_i Cp_i$ was evaluated.

5) From the mass fractions and molecular weights of the pseudo-components, the average molecular weight of the liquid mixture was calculated. The heat of reaction per kg of liquid mixture for the hydrocracking reaction was estimated as given in Section 4.6. The heat of reaction per kg of sulfur hydrogenated for the HDS reaction was also determined as detailed in Section 4.6.

6) Eqns. (4.11) through (4.13) were integrated numerically along the length of the catalyst bed using the Runge-Kutta-Gill method. The term $\sum_i m_i Cp_i$ was taken to be constant for each catalyst bed.

7) The reaction mixture exiting from each catalyst bed was quenched by the recycle gas. The purity of the quench stream was known. Using the density of the quench stream, the mass flow rate of the quench gas was calculated. The total gas flow rate was then the sum of the gas flow rate at the exit of the bed and the flow rate of the quench stream. In addition, from

TABLE 4.7 Thermodynamic Properties of the Pseudo-components in Vacuum Distillate

Comp no.	T_c K	P_c atm	V_c $cm^3/gmol$	ω	Mol. wt.
1	729.9	17.1	812.9	0.68	228
2	748.2	16.1	870.1	0.73	245
3	765.6	15.1	934.1	0.78	264
4	783.0	14.2	1000.4	0.83	284
5	800.9	13.4	1062.9	0.87	304
6	817.9	12.6	1133.2	0.92	326
7	834.9	11.8	1205.5	0.98	348
8	852.6	11.2	1272.8	1.02	369
9	870.2	10.6	1341.2	1.07	392
10	887.8	10.1	1410.7	1.12	414
11	905.3	9.6	1481.2	1.17	437
12	924.5	9.3	1536.1	1.21	458
13	942.8	8.9	1599.5	1.26	480
14	961.1	8.5	1663.4	1.30	501

the heat capacity data for hydrogen and methane, the heat capacity of the quench stream was also calculated. The inlet temperature of the reactants to the next bed was then calculated by an enthalpy balance.

8) Steps 6 and 7 were then repeated for each bed in the reactor. The total hydrogen consumed was then calculated as given in Section 4.9.

4.10.2 Kerosene

A single bed kerosene hydrodesulfuriser was simulated using the proposed model with a feed having a TBP cut of 430-558 K. The TBP curve for the feed is shown in Figure 4.2. Tri-substituted thiophene was taken as the model sulfur compound as it has a boiling point close to that of kerosene (Paushkin, 1962). A second order global rate constant assumed for this model taking the activation energy to be 150 kJ/kmol (Chu and Wang, 1982) is given below.

$$k_s = 5.7 \times 10^{12} \ e^{-18118/T} \qquad\qquad (4.33)$$

The catalyst specifications are same as those for vacuum distillate. Table 4.2 shows the feed specifications to the kerosene hydrodesulfuriser.

A step by step procedure for the solution of the model equations is given below.

Steps (1) and (2) are the same as those described for vacuum distillate in Section 4.10.1. The TBP data are given in Table 4.2 and the TBP curve is shown in Figure 4.2. The characteristics of the pseudo-components are given in Table 4.8

TABLE 4.8 Characterisation of the Pseudo-components in Kerosene

Component No.	Boiling Pt., K	Av.Boiling Pt., K	Sp. gravity	UOPK	Vol.%
1	388.6-408.6	398.6	0.743	12.1	4.0
2	408.6-428.6	418.6	0.761	12.0	5.0
3	428.6-448.6	438.6	0.777	11.9	9.0
4	448.6-468.6	458.6	0.790	11.9	12.0
5	468.6-488.6	478.6	0.803	11.9	15.5
6	488.6-508.6	498.6	0.813	11.8	16.5
7	508.6-528.6	518.6	0.824	11.9	14.0
8	528.6-548.6	538.6	0.834	11.9	9.5
9	548.6-568.6	558.6	0.846	11.8	5.0
10	568.6-588.6	578.6	0.858	11.8	7.0

and the plant data are shown in Table 4.9.

3) Using Eqns. (3.11) through (3.16), molecular weight, T_c, P_c, V_c and ω of the pseudo-components were calculated and are tabulated in Table 4.10.

4) Using the mass fraction and the molecular weight of the pseudo-components, the average molecular weight of the kerosene feed was calculated.

5) From the volumetric flow rate of the recycle and the make-up gas, molecular weight of hydrogen and methane and the purity of both these streams, the molar flow rate of the hydrogen gas mixture as well as its average molecular weight were calculated.

6) The total molar flow rate at the inlet of the reactor was the sum of the molar flow rate of the kerosene feed and the molar flow rate of the hydrogen gas mixture.

7) The composition of the feed stream was then expressed in terms of mole fraction based on the total molar flow rate. The sulfur content was also expressed in terms of mole fractions.

8) From the critical properties of hydrogen and methane taken from the literature and using Eqns. (4.5) and (4.6), the critical properties of the hydrogen gas mixture, which was taken as a single component, were calculated. Thus if N is the total number of pseudo-components in kerosene then (N+1) is the total number of components in the reaction mixture.

9) Using the T_c, P_c, V_c and ω values of all the components in the reaction mixture, the molar heat capacity of the reaction mixture was calculated as given in Section 3.2.4. The heat of reaction was calculated as given in Section 4.6.

10) Eqns. (4.17) and (4.18) were integrated numerically along the

TABLE 4.9 Plant Data for Kerosene Unit

Set	1	2	3
Reactor charge, m^3/h	83	73	75
Combined make-up H_2, Nm^3/h	1410	1650	1300
Recycle gas, Nm^3/h	250	nil	250
Reactor inlet temp., K	581	570	568
Reactor pressure, atm.	24	24	24
Sulfur in feed, wt.%	0.55	0.49	0.33
Catalyst volume, m^3	15.5	15.5	15.5
Make-up gas purity, vol.%	89	72	82
Recycle gas purity, vol.%	86	68	70
*Temperature rise across the reactor	2 to 5 K	2 to 5 K	2 to 5 K

* personal communication with plant personnel

TABLE 4.10 Thermodynamic Properties of Pseudo-components in Kerosene

Comp. no.	T_c K	P_c atm	V_c $cm^3/gmol$	ω	Mol. wt.
1	576.9	27.2	451.3	0.37	119
2	599.1	25.9	485.7	0.40	131
3	620.5	24.6	523.9	0.44	142
4	640.8	23.2	566.9	0.48	155
5	660.8	21.9	611.8	0.52	169
6	680.0	20.5	661.8	0.56	183
7	700.0	19.3	712.7	0.61	199
8	717.8	18.1	765.2	0.64	215
9	736.8	17.2	816.4	0.69	232
10	755.8	16.3	868.9	0.73	299

length of the reactor using the Runge-Kutta-Gill method. The total molar flow rate as well as the rate constants were calculated at each integration step. The sulfur concentration, effluent temperature, hydrogen consumption and the total molar flow rate at the exit of the reactor were calculated.

11) The hydrogen consumption was calculated as described in Section 4.9.

4.10.3 Diesel:

The proposed model was also used for the simulation of a single bed diesel hydrodesulfuriser. The diesel fraction had a boiling range of 493-688 K. Benzothiophene was taken as the model compound because it is more representative of sulfur compounds, as compared to thiophenes for heavier boiling petroleum fractions (Jewell et al., 1976). For HDS of diesel, plant data for two different types of catalysts were available and separate pre-exponential factors were used for the rate of HDS. However, only a single hydrocracking rate equation was used for both the catalysts. The expressions for the rate constants for the HDS reaction using the activation energy given by Frye and Mosby (1967) and for the hydrocracking reaction using the activation energy given by El-Kady (1979) are:

For Harshaw HT-400 E
$$k_s = 9.7 \times 10^9 \, e^{-15500/T} \qquad (4.34)$$

For Procatalyse HR-304
$$k_s = 6.5 \times 10^9 \, e^{-15500/T} \qquad (4.35)$$

$$k_c = 4.0 \times 10^5 e^{-13416/T}$$

(4.36)

The catalyst specifications for Harshaw HT-400E are given in Table 4.4. No information was available about Procatalyse HR-304 catalyst except the make.

A step by step procedure for the solution of the model equations is given below.

Steps (1) to (6) are the same as those described for kerosene in the previous section. The TBP data for diesel are given in Table 4.3 and the corresponding TBP curve is shown in Figure 4.2. The characteristics of the pseudo-components are given in Table 4.11. The plant operating data for the two types of catalysts are included in Table 4.12 and 4.13, whereas the thermodynamic properties calculated for the thirteen pseudo-components are presented in Table 4.14.

7) Using Eqns.(4.2) and (4.3), the vapour pressures of the pseudo-components at reaction conditions were calculated whereas the vapour-liquid equilibrium constants were estimated from Eqn. (4.4). For the (N+1)th component, which is the hydrogen gas mixture, it was not possible to estimate the VLE constants using Eqns. (4.2) and (4.3). Being a light gas, the K-value of hydrogen gas mixture is likely to be high. A value of 20 was assumed. Later calculations showed that the vapour and liquid flow rates were not sensitive to this value.

8) Eqns. (4.22) through (4.26) were used to calculate the vapour and liquid flow rates and concentrations.

9) The heat capacities of the liquid and vapour phases were

TABLE 4.11 Characterisation of the Pseudo-components in Diesel

Comp. no.	Boiling Range K	Mid-boiling Pt., K	Sp. Gr.	UOPK	Vol.%
1	493-508	500.5	0.814	11.9	1.5
2	508-523	515.5	0.824	11.8	3.0
3	523-538	530.5	0.833	11.8	3.0
4	538-553	545.5	0.842	11.8	5.5
5	553-568	560.5	0.849	11.8	11.0
6	568-583	575.5	0.855	11.8	12.0
7	583-598	590.5	0.862	11.8	14.0
8	598-613	605.5	0.869	11.8	13.5
9	613-628	620.5	0.876	11.9	14.0
10	628-643	635.5	0.883	11.9	11.5
11	643-658	650.5	0.890	11.8	5.0
12	658-673	665.5	0.897	11.8	3.5
13	673-688	680.5	0.904	11.8	2.5

TABLE 4.12 Plant Data for Diesel Unit Using Procatalyse HR - 304
　　　　　　　Catalyst (Set A)

Feed flow rate, kg/h	26067
Make-up gas, kg/h	401
Recycle gas, kg/h	2659
Reactor inlet temp., K	623
Reactor inlet pressure, atm.	37
Reactor outlet pressure, atm.	35
Sulfur in feed, wt.%	2.0
Overall composition of recycle and make-up gas, mol % :	
Hydrogen	67.3
Hydrogen sulfide	1.8
Methane	28.5
Ethane	2.1
Propane	0.3

TABLE 14.13 Plant Data for Diesel Unit Using Harshaw HT - 400E
Catalyst

Set	B1	B2	B3
Charge rate of diesel feed, m^3/h	29.4	34.5	37.3
Reactor inlet temperature, K	608	613	613
Make-up gas, Nm^3/h	2500	1525	1500
Recycle gas, Nm^3/h	7200	2900	3100
Reactor pressure, atm.	35	35	35
S in feed, wt.%	1.48	1.46	1.2
Catalyst volume, m^3	10	10	10
Recycle gas purity, vol. %	56	80	90
Make-up gas purity, vol. %	58	86	90

TABLE 4.14 Thermodynamic Properties of the Pseudo-components in Diesel

Comp. no.	T_c K	P_c atm.	V_c cm^3/mole	ω	Mol. wt.
1	681.8	20.4	666.6	0.563	185
2	696.7	19.6	701.1	0.593	196
3	711.2	18.8	737.0	0.624	208
4	725.4	18.0	776.6	0.656	220
5	739.0	17.2	819.1	0.670	233
6	752.5	16.4	863.2	0.725	247
7	765.9	15.6	908.4	0.760	261
8	779.3	14.9	954.1	0.795	275
9	792.7	14.3	1000.7	0.830	290
10	805.9	13.7	1048.2	0.866	305
11	819.3	13.1	1095.9	0.902	321
12	832.3	12.6	1145.9	0.939	336
13	845.3	12.0	1197.7	0.976	353

calculated by the procedure outlined earlier.

10) The heats of reactions for the HDS and hydrocracking reactions were calculated as given in Section 4.6.

11) Eqns. (4.19) through (4.21) were integrated numerically along the length of the reactor using the Runge-Kutta-Gill method. At each integration step, the vapour and liquid molar flow rates, the total molar flow rate, the moles of feed cracked, moles of sulfur hydrogenated, temperature of the reactor and the rate constants were calculated. The overall hydrogen consumption in the reactor was calculated as given in Section 4.9.

4.11 RESULTS AND DISCUSSION

The model equations were integrated along the length of the catalyst bed using the Runge-Kutta-Gill method. Each integration step was taken to be 1/25th of the catalyst bed which was found to be adequate after preliminary testing. The programs for the three hydrodesulfurisation units were written in Fortran IV. While the CPU time for vacuum distillate was one second, kerosene and diesel feeds took 7 and 11 seconds, respectively. The listings of these programs are given in Appendices B, C and D, respectively. For each unit, the sulfur content in the feed, the reactor temperature and the amount of feed hydrocracked (except for kerosene) were calculated at each integration step along the length of the catalyst bed. For diesel feed, the amounts of vapour and liquid at the end of each increment were also calculated.

4.11.1 Vacuum Distillate

Figure 4.3 shows the calculated temperature profile and
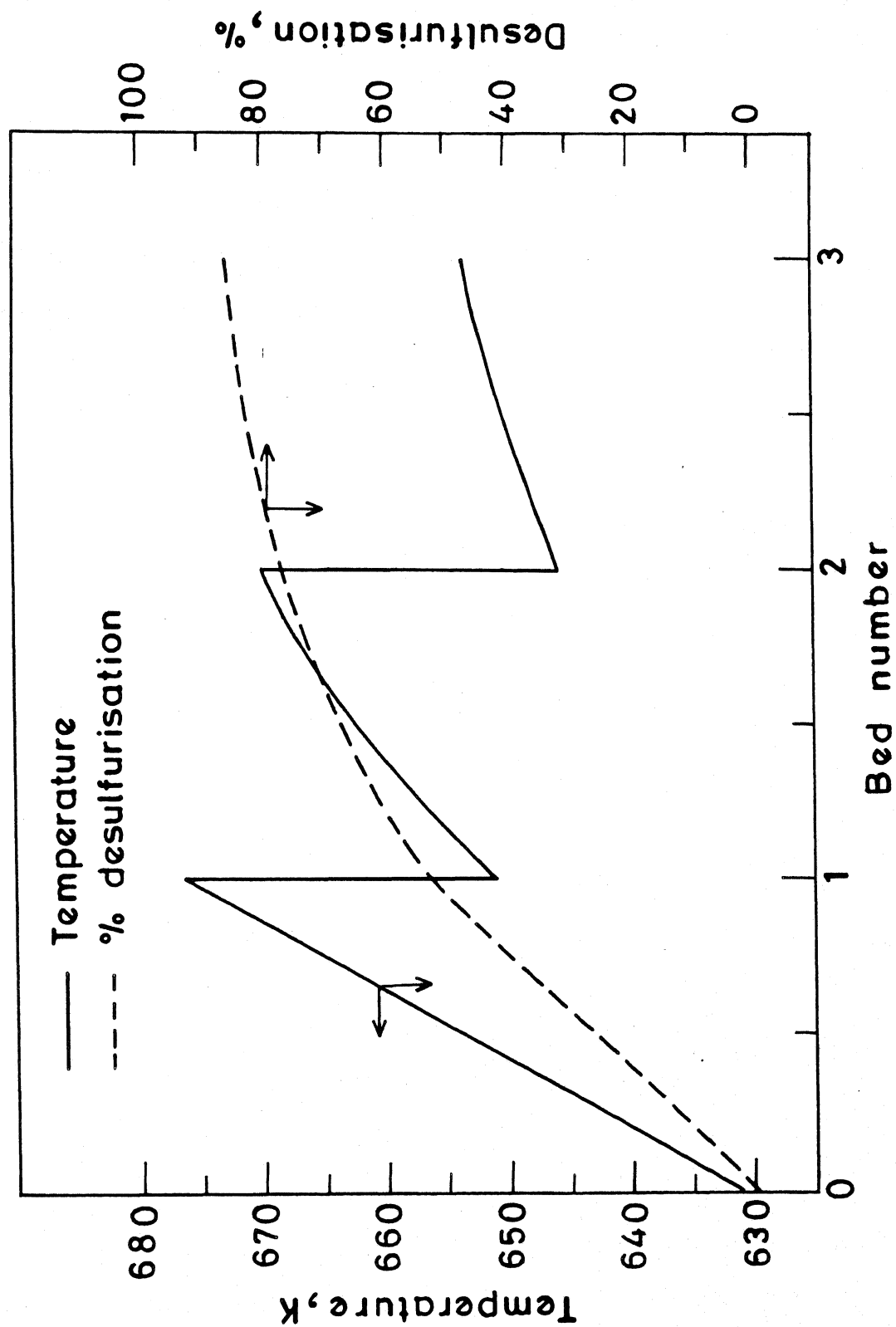
Fig. 4.3 Temperature and % desulfurisation profiles during HDS of Vacuum Distillate.

percent desulfurisation along the reactor length. The temperature drop between the beds is due to the intermediate quenching. As the sulfur concentration decreases, the rate of reaction also decreases and hence the temperature rise decreases from bed to bed. A comparison of the calculated results with the plant data is shown in Table 4.15. The only comparable data available from the plant are the temperature, percent desulfurisation, percent uncracked feed at the exit of the reactor and the hydrogen consumption. The agreement is generally good. The maximum discrepancy was in the prediction of the reactor exit temperature. Peng-Robinson's EOS was used for estimating the enthalpies which may not give accurate results for heavier feeds. A possible reason for the discrepancy in hydrogen consumption can be found in the assumption of a single compound to represent the sulfur compounds present in the feed.

The effect of variation in the reactor inlet temperature and sulfur content of the feed on the extent of desulfurisation, overall hydrogen consumption and the reactor exit temperature were also studied. The effect of inlet temperature and sulfur content of the feed is shown in Figures 4.4 and 4.5, respectively. As expected, an increase in the inlet feed temperature resulted in an increase in the rates of desulfurisation and hydrocracking reactions. An increase in the inlet temperature from 631 to 641 K, resulted in an increase in the exit temperature from 653.7 to 666.7 K and the desulfurisation from 85.6% to 90.8 wt.% . The corresponding increase in the cracked feed was from 4.1 to 6.9 wt.% and in the hydrogen consumption from 302 to 326 kg/h . Thus, the operating temperature is a compromise between the desulfurisation required and the extent of hydrocracking that can

TABLE 4.15 Comparison of Calculated Results with the Plant Data
for Vacuum Distillate

	Plant	Simulated	% error
S at the exitof the first bed, wt.%	-	1.61	-
Temp. at the exit of the first bed, K	-	676.5	-
Temp. at the inlet of the second bed, K	-	650.7	-
S at the exit of the second bed, wt.%	-	0.80	-
Temp. at the exit of the second bed, K	-	670.0	-
Temp. at the inlet of the third bed, K	-	646.4	-
S at the exit of the third bed, wt.%	0.51	0.49	-0.76
Temp. at the exit of the third bed, K	656.0	653.8	
Temp. rise across the reactor, K	25	22.8	-8.8
H_2 consumption, kg/h	316	302	-4.4
Uncracked feed, wt.%	96.0	95.9	-0.146
Desulfurisation, wt.%	85.0	85.6	+0.76
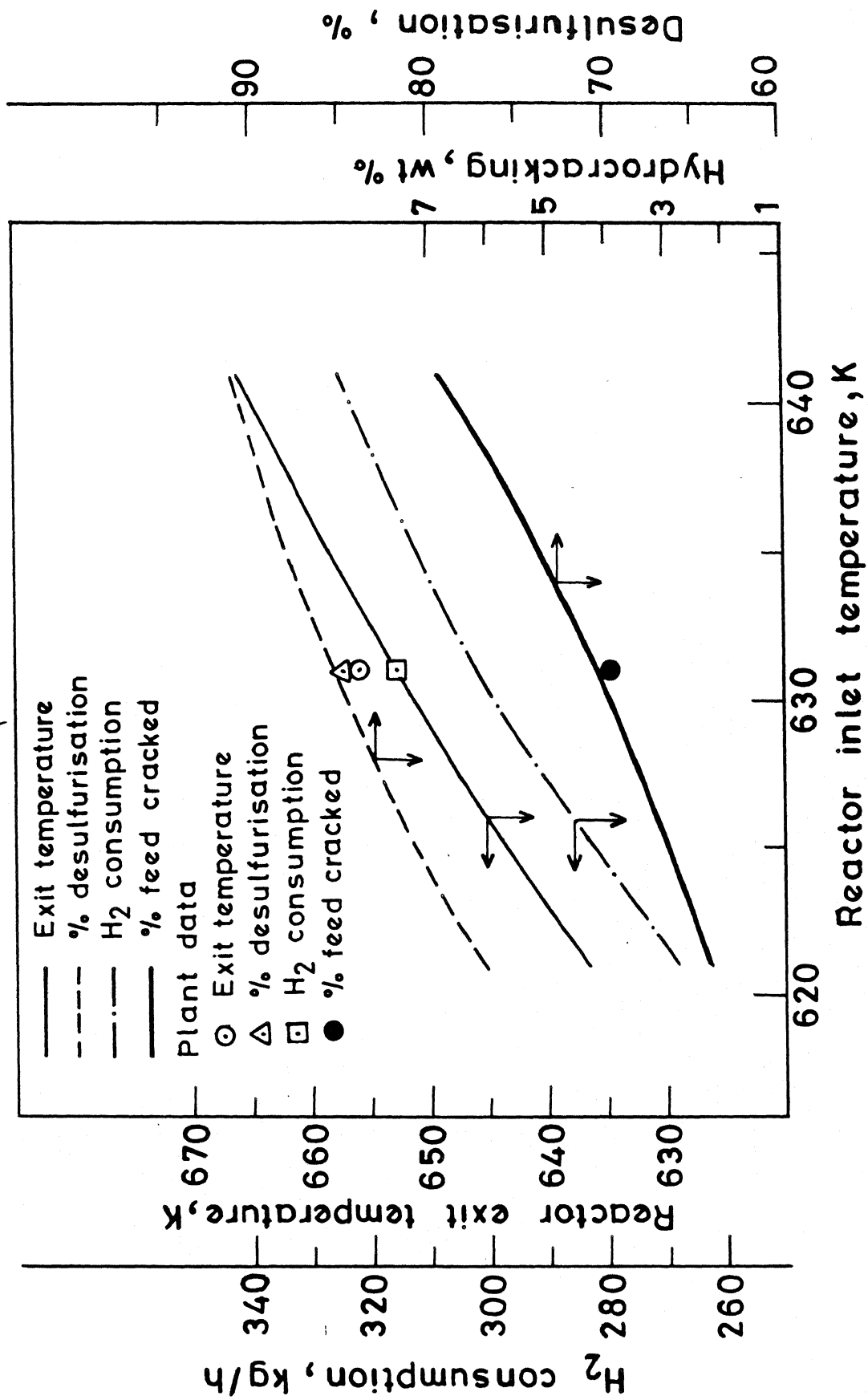
Fig. 4.4   Effect of inlet temperature on reactor performance during HDS of Vacuum Distillate.
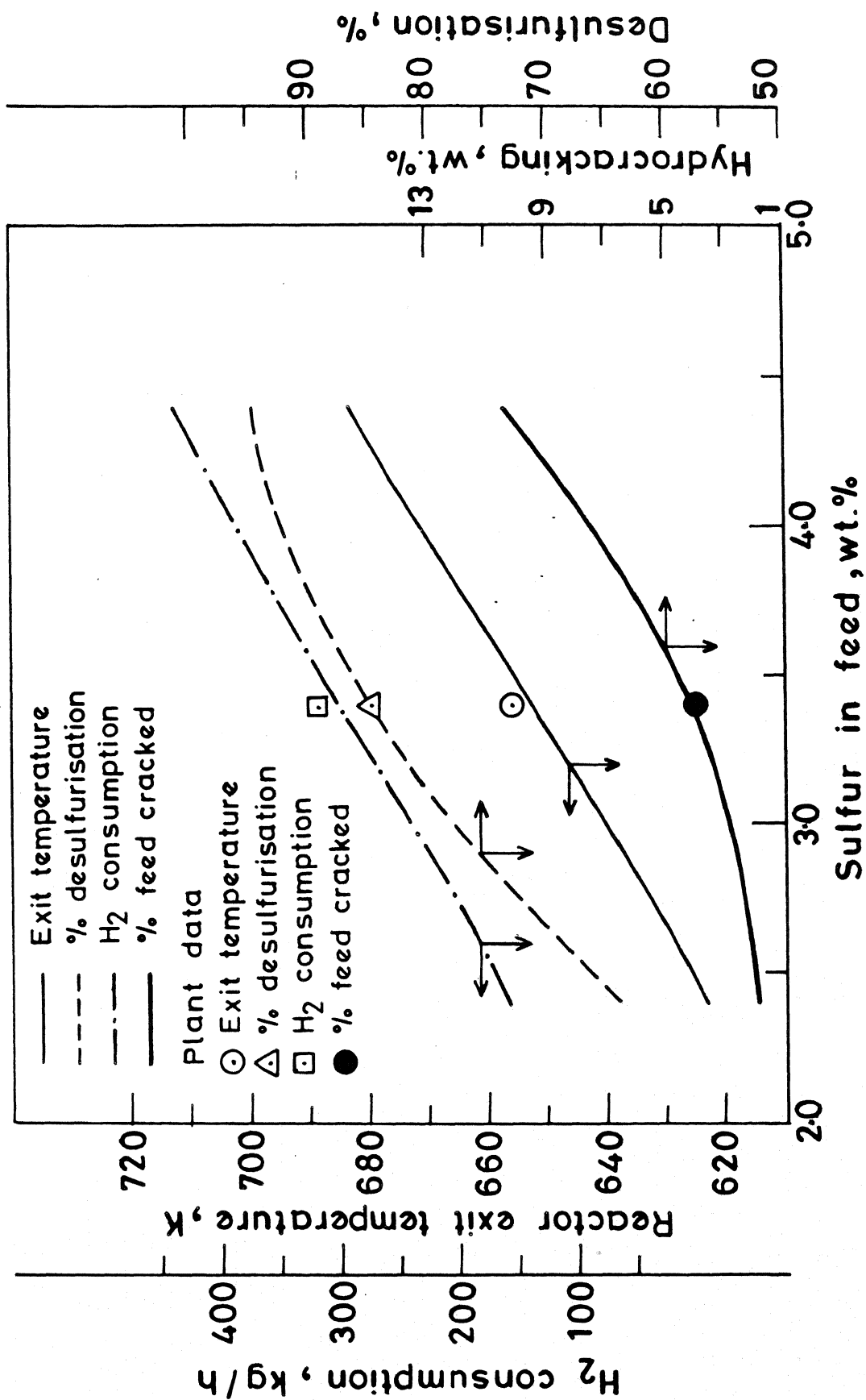
Fig. 4.5 Effect of sulfur in feed on reactor performance during HDS of Vacuum Distillate feed.

be tolerated.

An increase in the sulfur content of the feed from 3.4 to 4.4 wt.%, increased the reactor temperature because of the increase in the rate of HDS (Figure 4.6). This temperature rise, in turn, increased the rate of hydrocracking and further increased the rate of desulfurisation. As a result, the extent of desulfurisation increased from 85.6 to 95.2 wt. % for a one percent increase in feed sulfur content. A comparison of Figures 4.3 and 4.6 shows that the temperature rise in the first bed for feed containing 4.4 wt.% of sulfur is 85 K whereas for the normal case it is only 46 K. However, the temperature rise in the second and third beds is lower for the higher sulfur content feed. This is attributed to the fact that because of the higher temperature and sulfur concentration, most of the desulfurisation is completed in the first bed resulting in low rates of desulfurisation reaction in the subsequent beds. The corresponding increase in the cracked feed was from 4.1 to 10.5 wt.% . Hydrocracking reaction being first order was affected less than the desulfurisation reaction.

4.11.2 Kerosene

For kerosene, on the same catalyst (HT - 400E), three sets of data were available (Table 4.9). The temperature and extent of desulfurisation along the reactor for Set 3 is shown in Figure 4.7. The profiles for Sets 1 and 2 were similar and have not been shown. Since the reactor has been assumed to be adiabatic, both the reactor temperature and the extent of desulfurisation increase along the reactor length. A comparison of the calculated results and the plant data for all the three sets
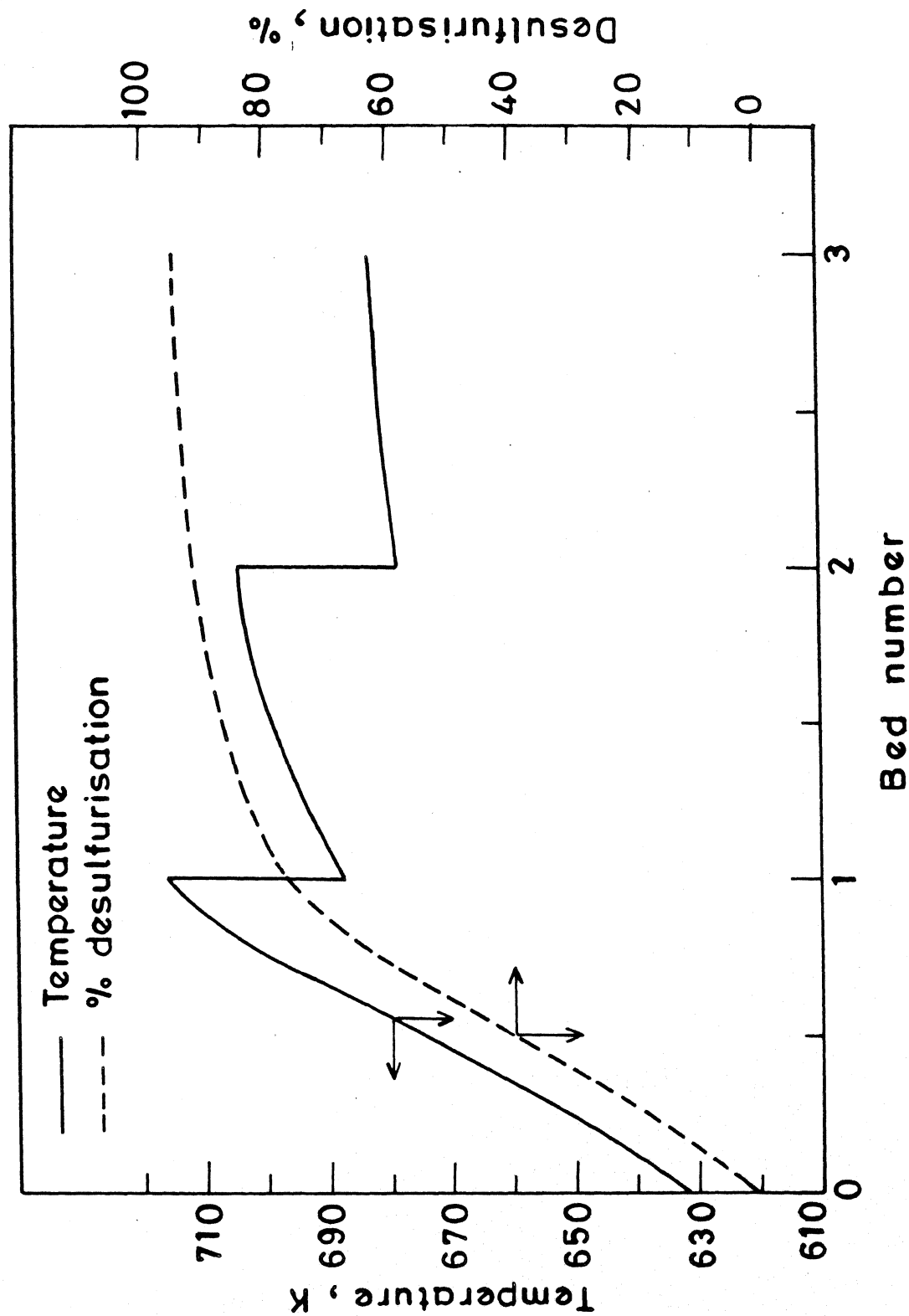
Fig.4.6 Temperature and % desulfurisation profiles during HDS of Vacuum Distillate (4.4 wt% sulfur in feed).
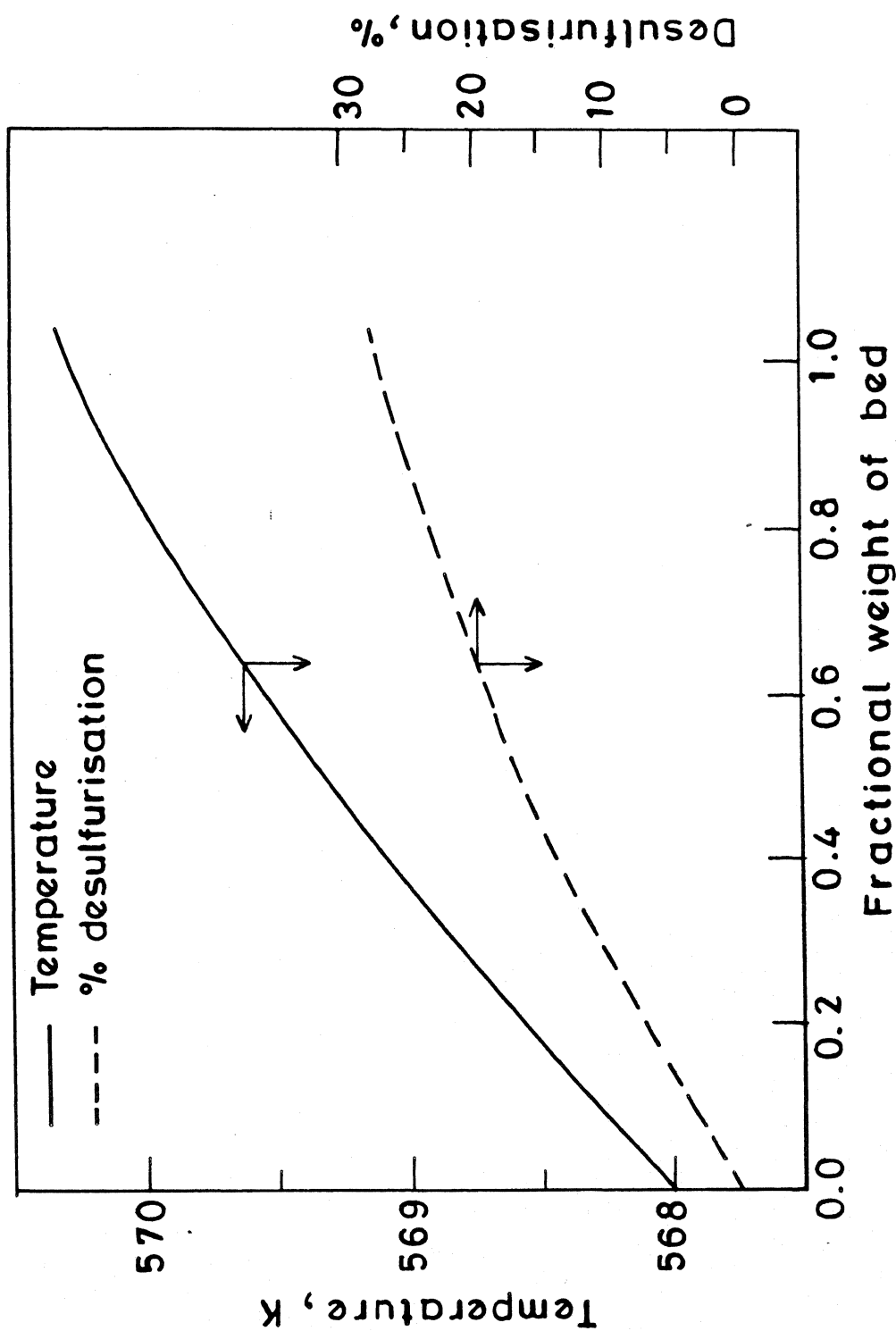
Fig.4.7 Temperature and % desulfurisation profiles during HDS of Kerosene feed (set 3).

is shown in Table 4.16. The discrepancy in predicting the extent of desulfurisation at the exit is a maximum of 5.9%. Except for Set 1, the temperature rise is within the specified limits.

The effect of a change in reactor inlet temperature or sulfur content of the feed on the reactor performance was also studied for the 3rd set of operating data and are shown in Figures 4.8 and 4.9, respectively. By increasing the reactor inlet temperature from 568 to 578 K, the desulfurisation increased from 28.5 to 39.4 wt. % whereas the reactor exit temperature increased from 570.3 to 581.2 K. An increase in the sulfur content of the feed from 0.33 to 0.53 wt.% resulted in an increase in the reactor exit temperature from 570.3 to 573.6 K. The extent of desulfurisation increased from 28.5 to 42.5 wt. % and the hydrogen consumption from 14.2 to 34.1 kg/h. Since the sulfur content of the feed is low, the temperature rise across the reactor is small.

4.11.3 Diesel

For the diesel feed, plant data were available for two types of catalysts. While Set A was for Procatalyse HR 304, the other 3 sets (B1, B2, B3) were for Harshaw HT-400E. The temperature and extent of desulfurisation profiles along the length of the reactor for Set B1 are shown in Figure 4.10. The profiles for all the other sets were also similar and hence have not been shown. A comparison of the calculated results and the plant data for set A and set B is shown in Table 4.17A and 4.17B, respectively. The percent desulfurisation matched quite well in all the four cases, the maximum deviation being 5 %. The hydrogen consumption and the percent desulfurisationfor Set A deviated by 19.2 and 4.9 %, respectively from the plant data. A possible

TABLE 4.16 Comparison of Calculated Results with Plant Data for Kerosene Feed

Set	1			2			3		
	Plant	Calc.	% error	Plant	Calc.	% error	Plant	Calc	% error
Reactor exit temp., K	583-586	588.9	–	572-575	575.1	–	570-573	570.3	–
Desulfurisation, wt.%	56.4	56.9	0.9	42.9	41.4	-3.3	30.3	28.5	-5.9
H_2 consumption, kg/h	–	52.5	–	–	29.9	–	–	14.2	–
Moles at the outlet, kmol/h	–	434	–	–	396	–	–	406.6	–
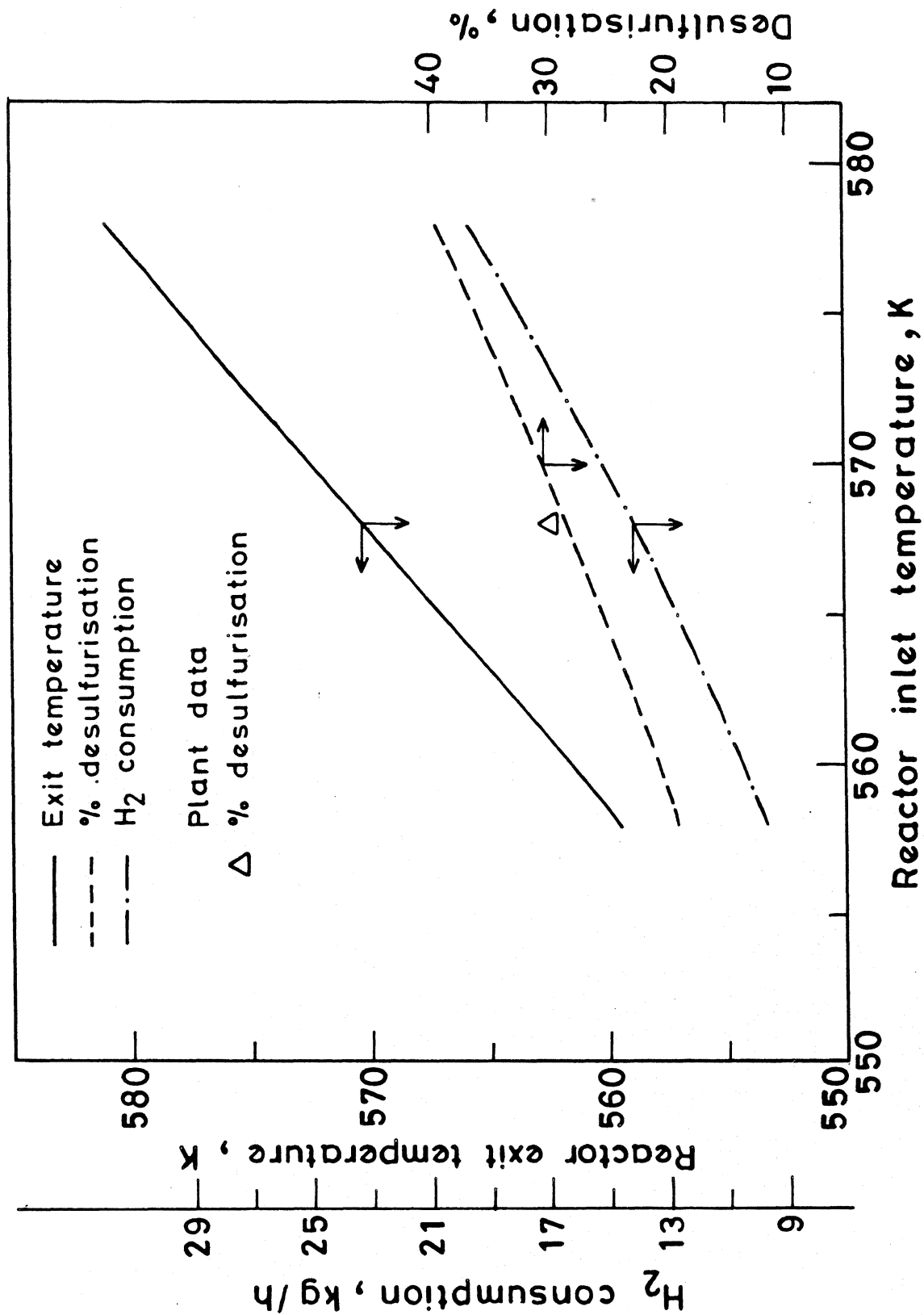
Fig. 4.8   Effect of inlet temperature on reactor performance
during HDS of Kerosene feed (set 3).
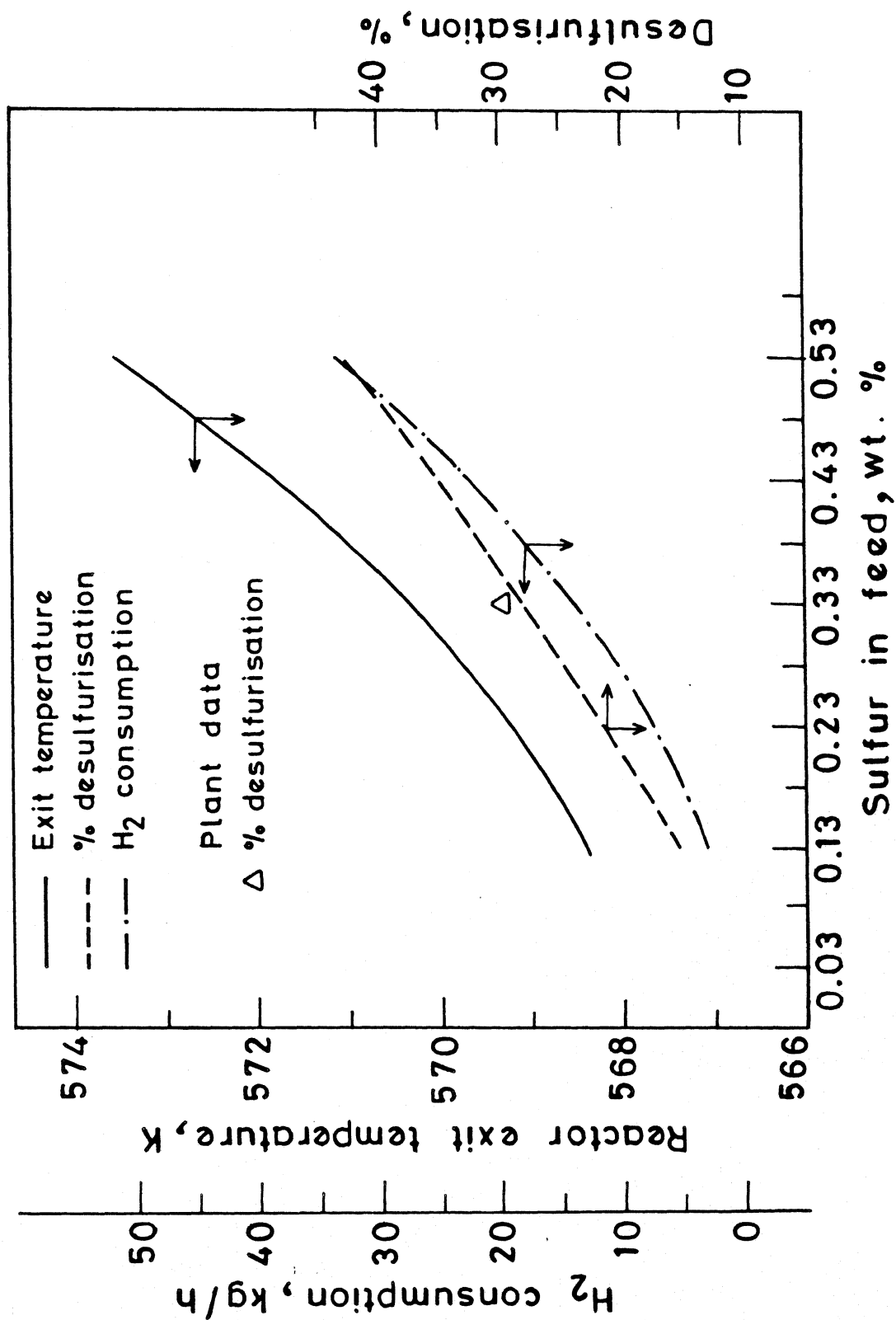
Fig. 4.9 Effect of sulfur in feed on reactor performance during HDS of Kerosene feed (set 3).
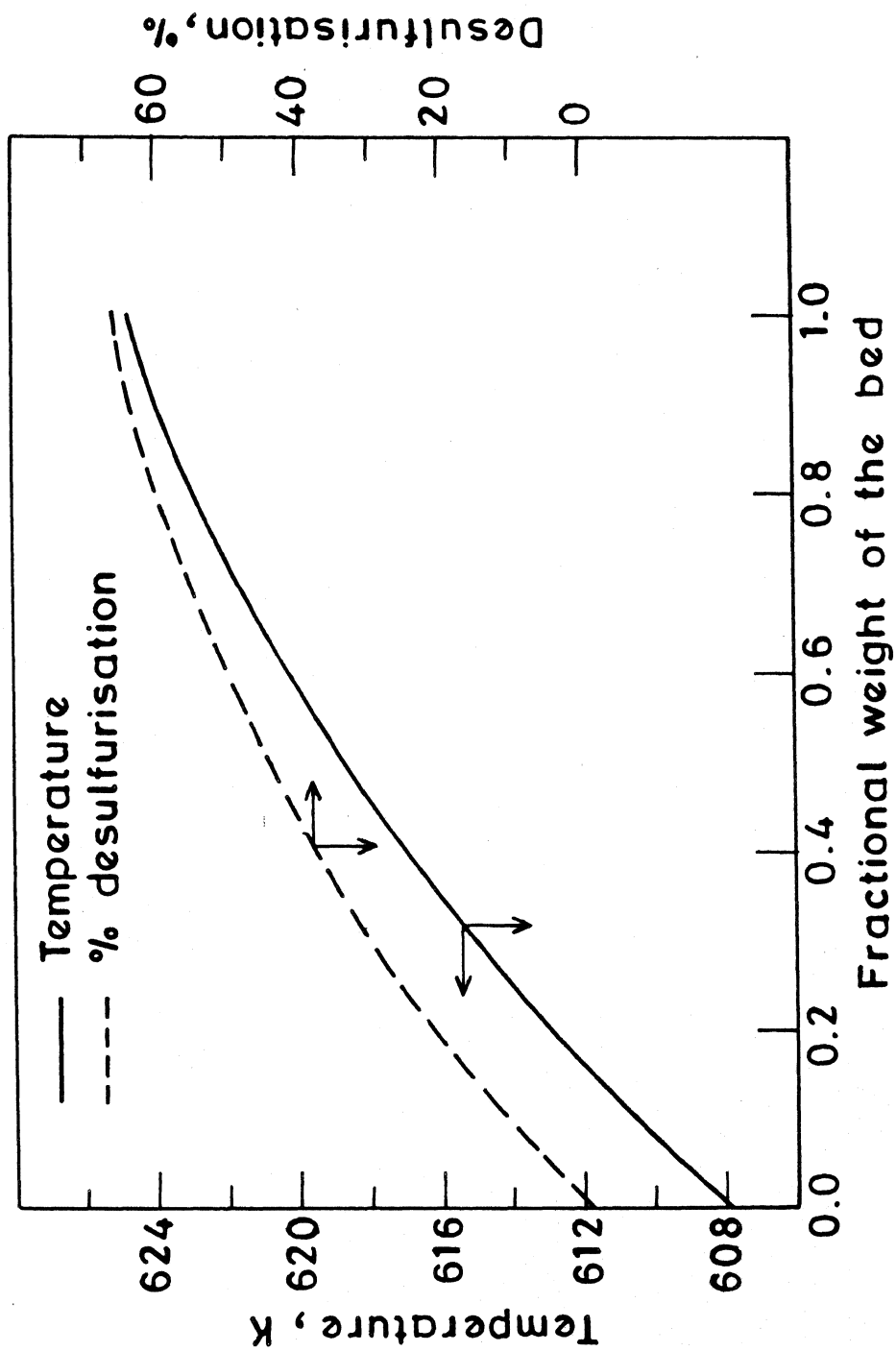
Fig.4.10 Temperature and % desulfurisation profiles
during HDS of Diesel feed (set B1)

TABLE 4.17A Comparison of Calculated Results with Plant Data for Diesel Feed (Procatalyse HR-304 Catalyst)

	Set A		
	Plant	Calc.	% error
Exit reactor temp., K	649.0	652.5	
Temp. rise across the reactor, K	26	29.5	13.4
H_2 consumption, kg/h	109	88.0	-19.2
Desulfurisation, wt.%	90	85.55	-4.9
V/F ratio at the inlet	0.848	0.8472	-0.09
V/F ratio at the exit	0.899	0.8683	-3.3
Moles at the outlet, kmol/h	473.0	488.0	3.2
Uncracked feed, wt. %	96.38	97.81	1.5

TABLE 4.17B Comparison of Calculated Results with Plant Data for Diesel Feed (HT-400E Catalyst)

	B1			B2			B3		
	Plant	Calc.	% error	Plant	Calc.	% error	Plant	Calc.	% error
Exit reactor temp., K	–	624.6	–	–	630	–	–	625.0	–
H_2 consumption, kg/h	–	46.9		–	48.6	–	–	35.4	–
Desulfurisation, wt.%	67.6	65.5	-3.1	60.96	58.15	-4.6	49.16	47.5	-3.4
V/F ratio at the inlet	–	0.8522		–	0.6602	–	–	0.6502	–
V/F ratio at the exit	–	0.8591		–	0.6482	–	–	0.6426	–
Moles at the outlet, kmol/h	–	510.7		–	293.0	–	–	312.0	–
Uncracked feed, wt.%	–	98.9		–	98.9	–	–	99.1	–

reason for this discrepancy could be due to the assumption that desulfurisation in the vapour phase is negligible. For the other sets, these could not be compared due to lack of plant data. Although the calculated V/F ratio at the inlet of the reactor was in good agreement with the plant data; at the exit, the deviation was approximately 3.3 %. The discrepancy may be due to the ideal K values used in the calculation of the V/F ratio in this model. Since the reactor exit temperature is higher than that at the inlet, a higher V/F ratio is expected at the exit. This was found to be valid for Sets A and B1. However, for Sets B2 and B3, the calculated V/F ratio at the exit is somewhat lower than that at the inlet and this may be attributed to a larger uncertainty in estimation of this ratio because of smaller vapour fractions in these cases ($\sim$ 0.65) as compared to the other sets ($\sim$ 0.85). The error in predicting the weight percent feed cracked was 1.5 for Set A. The molar flow rate at the exit of the reactor deviated by 3.2 % for the same set.

The effect of variation in the reactor inlet temperature or sulfur content of feed for Set B1 was also studied as for the previous two HDS models and are shown in Figures 4.11 and 4.12, respectively. Thus, by increasing the reactor inlet temperature from 608 to 618 K, the reactor exit temperature increased from 624.6 to 638.3 K, the percent desulfurisation increased from 65.5 to 79.4, hydrogen consumption increased from 46.9 kg/h to 57.5 kg/h and weight percent cracked feed , from 1.1 to 1.66. The exit temperature, percent desulfurisation, percent feed hydrocracked as well as the hydrogen consumption increased gradually with an increase in the reactor inlet temperature. However, the percentage change is lower than that for vacuum distillate and higher than
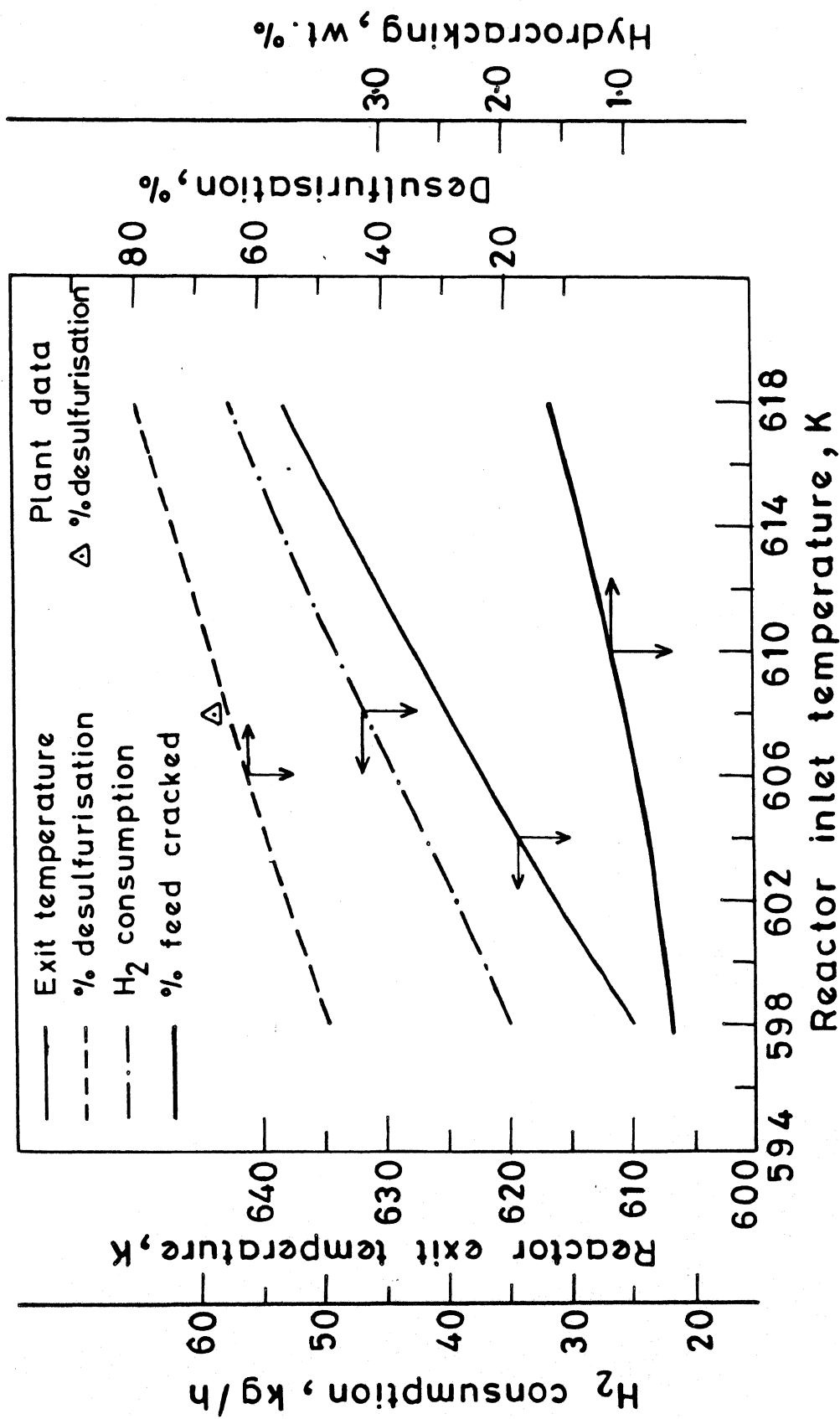
Fig. 4.11   Effect of inlet temperature on the reactor performance during HDS of Diesel feed (set B1)
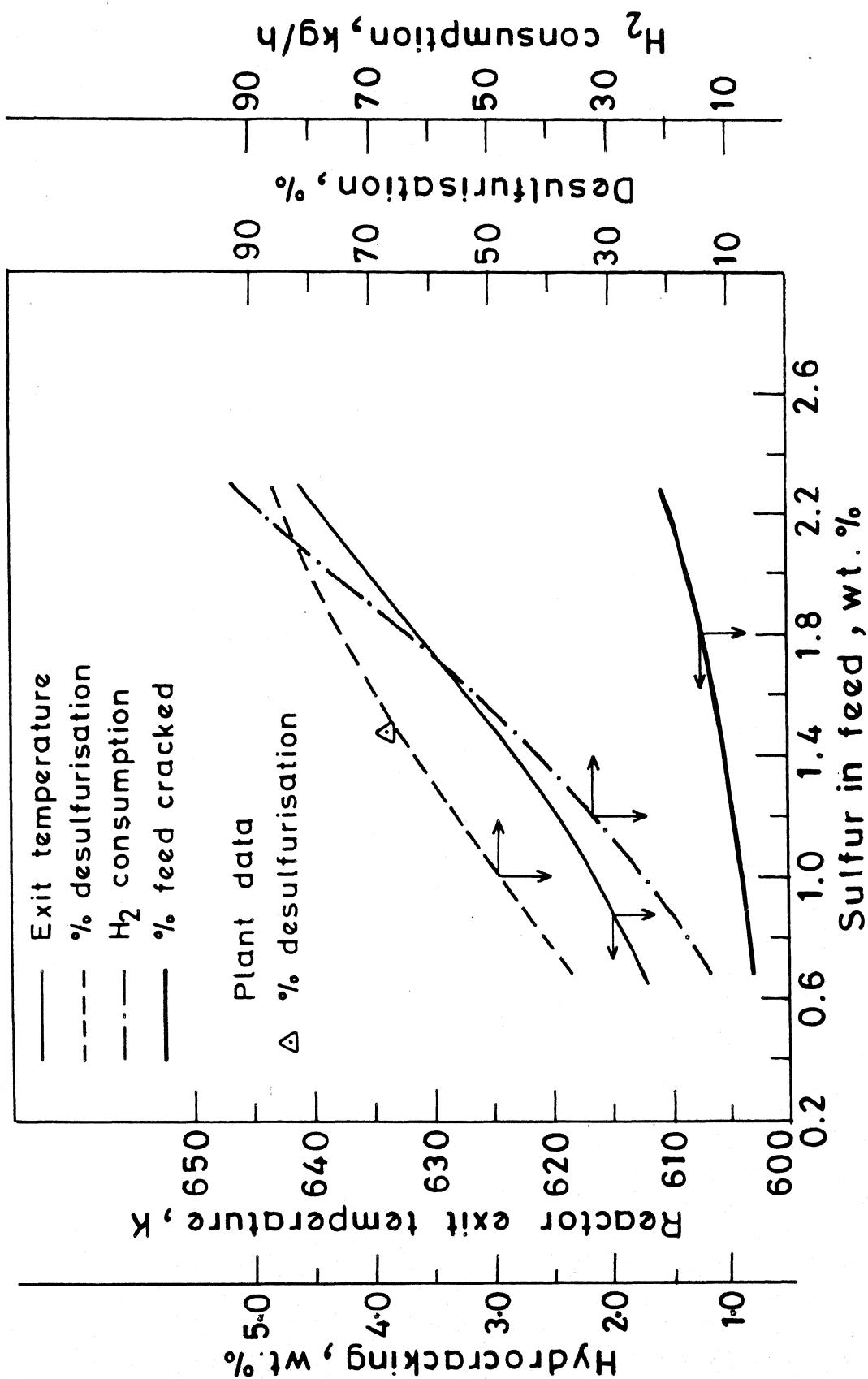
Fig. 4.12 Effect of sulfur in feed on reactor performance during HDS of Diesel feed (set B1)

that for kerosene because of the sulfur content of the diesel was between the two.

By increasing the sulfur content of the feed from 1.2 to 2.28 wt. %, the reactor exit temperature increased from 624.6 to 641.6 K, percent desulfurisation increased from 65.5 to 85.5 wt.%, hydrogen consumption increased from 46.9 to 93.2 kg/h and weight percent feed hydrocracked from 1.1 to 1.57. The trend is similar to that observed for other feedstocks.

BIBLIOGRAPHY

Agrawal, B. B.; Rohatgi, H.S.; Gulati, I.B. "Nature and Distribution of Sulphur Compounds in Darius Crudes" J. Inst. Pet., 59 (569), 133-138, 1973

Agrawal, B. B.; Rizvi, S.A.A.; Gulati, I.B. "Sulphur Compounds in Rostam Crude Oil" Ind. J. Tech., 14, 301-303, 1976.

Birch, S.F.; Cullum, T.V.; Dean, R.A.; Deyner, R.L. "Sulphur Compounds in Kerosene Boiling Range of Middle East Crudes", Ind. Eng. Chem., 47(2), 240-249, 1955.

Chu, C.I.; Wang, I. "Kinetic Study on Hydrotreating", Ind. Eng. Chem. Process Des. Dev., 21, 338-344, 1982.

El-Kady, F.Y. "Hydrocracking of Vacuum Distillate Over Bifunctional Molybdenum-Nickel / Silica-Alumina Catalyst", Ind. J. Tech., 17, 176-183, 1979.

Frye, C.G.; Mosby, J.F. "Kinetics of Hydrodesulfurisation", Chem. Eng. Progress, 63(9), 66-70, 1967.

Hoog, H. "Catalytic Hydrodesulfurisation of Gas Oil: Analysis of the Kinetics of the Reaction" J. Inst. of Petrol., 36, 738-751 , 1950.

Houlla, M.; Broderick, D.H.; Sapre, A.V.; Nag, N.K.; de Beer, V.H.J.; Gates, B.C.; Kwart, H. "Hydrodesulfurisation of Methyl-Substituted Dibenzothiophene Catalysed by Sulfided Co-Mo/ γ-Al$_2$O$_3$" J. Catal., 61(2), 523-527, 1980.

Jaffe, S.B. "Hot Spot Simulation in Commercial Hydrogenation Processes" Ind. Eng. Chem. Process Des. Dev., 15(3), 410-416, 1976.

Kesler, M.G., Lee, B.I. "Improve Prediction of Enthalpy of Fractions" Hydrocarbon Processing, 55(3), 153-158, 1976.

Lee, B.I.; Kesler, M.G. "A Generalised Thermodynamic Crrelation Based on Three- Parameter Corresponding States" AIChE J., **21**(3) 510-527, 1975.

Papayannakos, N. "Kinetics of Catalytic Hydrodesulfurisation of a Deasphalted Oil and of the Asphaltenic and Non-Asphaltenic Fractions of a Petroleum Residue" Appl. Catal.; **24**(1-2), 99-107, 1986.

Paushkin, Y.M. "The Chemical Composition and Properties of Fuels for Jet Propulsion" Pergamon Press, 1962.

Peng, D.Y.; Robinson, D.B. "A New Two- Constant Equation of State" Ind. Eng. Chem. Fundam, **15**, 59-64, 1976.

Philippopoulos, C.; Papayannakos, N. "Intraparticle Diffusional Effects and Kinetics of Desulfurisation Reactions and Asphaltenic Cracking During Catalytic Hydrotreatment" Ind. Eng. Chem. Res., **27**(3), 415-420, 1988.

Qader, S.A.; Hill,G.R. "Hydrocracking of Gas Oil" Ind. Eng. Chem. Process Des. Dev., **8**(1), 98-105, 1969.

Reid, R.C.; Prausnitz, J.M.; Sherwood, T.K. "Properties of Gases and Liquids" 3rd Ed., McGraw Hill Book Co., 1977.

Sapre, A.V.; Gates, B.C. "Hydrogenation of Aromatic Hydrocarbons Catalysed by Sulfided $CoO-MoO_3/\gamma- Al_2O_3$ – Reactivities and Reaction Networks" Ind. Eng. Chem. Process Des. Dev., **20**, 68-73, 1981.

Schuit, G.C.A.; Gates, B.C. "Chemistry and Engineering of Hydrodesulfurisation " AIChE J., **19**(3), 417-445, 1973.

Smith, J.M.; Van Ness, H.C. "Introducton to Chemical Engineering Thermodynamics" McGraw Hill, New York,1984.

Soave, G. "Equilibrium Constants from a Modified Redlich-Kwong Equation of State" Chem. Eng Sci., **27**, 1197-1203, 1972.

Vargaftik, N.B. "Tables on the Thermophysical Properties of Liquids and Gases", Hemisphere Publishing Corp., John Wiley and Sons, Inc., 1975.

Walas, S.M. "Phase Equilibrium in Chemical Engineering" Butterworth Publishers, 1985.

CHAPTER - 5

CONCLUSIONS AND RECOMMENDATIONS

5.1 CONCLUSIONS

Reactor models for the hydrocracking and hydrodesulfurisation processes have been developed. These models require a limited number of inputs for predicting the reactor performance. The inputs required for the hydrocracking model are the TBP data, specific gravity data, flow rates and reactor conditions at the inlet. For the HDS models, in addition to the inputs required for the hydrocracking model, the sulfur content of the feed is also required. Inspite of the several simplifying assumptions, the model prediction were in good agreement with the available plant data. The hydrocracking model can predict the temperature profile along the length of the reactor, the yields of different products and the hydrogen consumption. The hydrodesulfurisation model predicts the temperature and percentage desulfurisation along the length of the reactor, the weight percent feed hydrocracked in the reactor and the overall hydrogen consumption. Due to lack of plant data, extensive validation of these models was not possible.

5.2 RECOMMENDATIONS

1) To improve the hydrocracking model, intrinsic kinetic data should be obtained experimentally on narrow boiling fractions.

Moreover, the effect of hydrocarbon type in the rates and product distribution should also be investigated.

2) Catalyst deactivation data should be obtained from the plant.

3) Extensive plant data is necessary for obtaining a generalised hydrocracking model.

4) Information on the sulfur distribution in the feed, together with rate of HDS for these compounds, should be obtained to improve the model.

PROGRAM DESCRIPTION FOR THE HYDROCRACKER MODEL

1) USAGE

The program evaluates the product distribution as well as the temperature at the exit of the first stage and second stage of a two-stage VGO hydrocracker. The MAIN program initialises certain variables, calls the major subroutine DGIL along with subroutines HTRXN and STENTH. The subroutine DGIL is called several times for the second stage in order to get convergence for the recycle stream. There are altogether eleven subroutines all in FORTRAN.

2) SUBROUTINES REQUIRED

SUBROUTINE DGIL: This major subroutine uses other subroutines like MIXCRI, to calculate the mixture critical properties, ENTHL, to calculate the rate constants at different temperatures, COENTH, to calculate the difference in enthalpy of the products and the reactants at reaction temperature and pressure. The differential heat and mass balance equations are solved using the Runge-Kutta-Gill method.

SUBROUTINE KINDAT: This subroutine calculates the rate constants for the different reactions at every step as a function of temperature.

SUBROUTINE PROP: This subroutine estimates the molecular weight, critical temperature, critical pressure, critical volume, acentric

factor and compressibility factor of the different fractions using the Lee-Kesler´s correlations.

SUBROUTINE MIXCRI: This subroutine calculates the critical properties of the mixture when the component critical properties are known.

SUBROUTINE HTRXN: This subroutine estimates the heat of reaction for all the reactions on the basis of hydrogen consumed.

SUBROUTINE PRODIS: This subroutine uses the Stangeland´s model to predict the product distribution for the different components which undergo cracking.

SUBROUTINE ENTHL:This subroutine uses the subroutine PHILN to calculate the enthalpy of a mixture at reaction temperature and pressure.

SUBROUTINE COENTH: This subroutine uses the subroutine PHILN to calculate the difference in enthalpy of the products and the reactants for all the reactions at reaction temperature and pressure.

SUBROUTINE PHILN: This subroutine calculates the fugacity coefficient and partial fugacity co-efficient for a pure component and a mixture respectively based on Peng Robinson´s equation of state.

SUBROUTINE CUBEQ: This subroutine evaluates the three roots of a cubic equation analytically.

SUBROUTINE STENTH: This subroutine calculates the difference in the enthalpy of the products and the reactants for all the reactions at standard temperature and pressure.

3) DESCRIPTION OF THE PARAMETERS

MAIN:

V	volumetric composition of the feed, %
SG	specific gravity of the components in feed at 60 $^{\circ}F$
FV	volumetric flow rate of the components in feed, m^3/h
FM	component mass flow rate, kg/h
P	product distribution in terms of mass fraction for all the reaction
FT	Total volumetric flow rate, m^3/h
CC	mass fraction of the components in feed or product
TB	mid boiling point of the pseudo-components, $^{\circ}C$
AK	reaction rate constant of different reactions
API	API gravity of the components
R1	carbon-to-hydrogen ratio of the components
FM2	component mass flow rate of the heavier products from the first stage fed to the second stage, kg/h
FM3	component mass flow rate of the feed to the second stage, kg/h
AMOL	molecular weight of the components
HRT	heat released during each reaction, kcal/kg H_2
TC	critical temperature of the components, K
PC	critical pressure of the components, atm
VC	critical volume of the components, $cm^3/$ gmole
OMEGA	acentric factor of the components
TRW	mass of the reactant(oil) required to yield unit mass of the cracked product, kg
HW	mass of hydrogen required to yield unit mass of the cracked product for each reactions, kg
RNTH	difference in enthalpy of the products and the

reactants at standard temperature and pressure, kcal/kg

N   total number of components in the mixture

M1   component number of the lightest component which undergoes cracking

N2   number of steps of integration for each bed

B   a parameter in Stangeland's model which determines the nature of the product distribution curve

C1   a parameter in Stangeland's model which determines the weight fraction of C4 and lighter fractions formed

RHOB   density of catalyst bed, kg/m^3

SUMF   mass flow rate of the feed to the first stage, kg/h

WHYI   hydrogen content of the petroleum feed at the reactor inlet, kg/h

TEMP   inlet or outlet temperature of the feed or product stream, K

STEMP   the standard temperature ie. 25 ^{o}C

HPM   hydrogen flow rate per cubic meter of feed at the inlet of the reactor, $Nm^3/$ (h) (m^3feed)

A2   factor in the calculation of the rate constants

VH   hydrogen flow rate at the inlet of each bed, Nm^3/h

N1   number of beds in the first stage

RHOH   density of hydrogen at normal temperature and pressure, kg/Nm^3

VCAT   volume of the catalyst per bed, m^3

CPH   heat capacity of hydrogen at reaction temperature and pressure, kcal/kg K

PT   average reactor pressure, atm

ICON   =1 if the temperature after every step increase is to be printed, otherwise, 2

QUENCH	volume of hydrogen used for quenching the products between the beds, Nm^3/h
WH	mass flow rate of hydrogen, kg/h
WHYE	hydrogen content of the petroleum product at the exit of the reactor, kg/h
FMCP	product of mass flow rate and the specific heat of the mixture, kcal/(h) (K)
T2	outlet temperature of each bed, K
FHCP	heat content of the quench stream for stage ´1´, kcal
TH2	temperature of the quench stream, K
REC	mass flow rate of the liquid product fed to the second stage, kg/h
RECC	mass fraction of the liquid product fed to the second stage
HSD	flow rate of the high speed diesel(HSD) fraction produced in the first stage, kg/h
HSDC	mass fraction of HSD fraction
ATF	flow rate of aviation turbine fuel(ATF) fraction produced in stage 1, kg/h
ATFC	mass fraction of ATF fraction
HNH	flow rate of the fraction boiling between C_4-140 ^oC, kg/h
HNHC	mass fraction of HNH
C4L	flow rate of C4 and lower fraction produced in stage 1, kg/h
C4LC	mass fraction of C4L
SUMF2	feed to the second stage from stage 1 (ie. REC), kg/h
FM2	component mass flow rate to the second stage from first stage, kg/h

CC2   mass fraction of the components to the second stage from stage 1

RHO2   density of the oil fed to the second stage from stage 1

FTS   total volumetric flow rate to the second stage, m^3/h

SUM2   total mass flow rate to the second stage, kg/h

N1   number of beds in the second stage

FHCP1   product of the mass flow rate and heat capacity of the quench stream for the second stage

SUMF3   mass flow rate of the recycle stream from the second stage, kg/h

RHO3   density of the recycle stream from the second stage, kg/m^3

NR   iteration number

SUM   calculated total mass flow rate to the second stage, kg/h

CN   calculated mass fraction of each component in the recycle stream from second stage

REC1   mass flow rate of the recycle stream from the second stage, kg/h

REC1C   mass fraction of the recycle stream to the second stage

HSD1   mass flow rate of HSD from the second stage, kg/h

HSD1C   mass fraction of HSD from second stage

C4L1   mass flow rate of C4 and lighter fractions, kg/h

C4L1C   mass fraction of C4 and lighter fractions

ATF1   mass flow rate of ATF from second stage, kg/h

ATF1C   mass fraction of ATF from second stage

HNH1   mass flow rate of the fraction boiling between C4-140°C

	from second stage, kg/h
HNH1C	mass fraction of naphtha from second stage
RECT	total feed to the second stage (recycle from first stage + recycle from second stage), kg/h
HSDT	total flow rate of HSD from first and second stage, kg/h
HNHT	total flow rate of HNH from first and second stage, kg/h
ATFT	total flow rate of ATF from first and second stage, kg/h
C4LT	total flow rate of C4 and lower fraction, kg/h
HSDTC	mass fraction of HSD based on total products from stage 1 and stage 2
HNHTC	mass fraction of HNH based on total products from stage 1 and stage 2
ATFTC	mass fraction of ATF based on the total products formed stage 1 and stage 2
C4LTC	mass fraction of C4 and lower fractions based on total product from stage 1 and stage 2

SUBROUTINE DGIL:

CCØ	component mass fraction
BV	volume of the catalyst, m^3
TEMP1	temperature of the mixture, K
AKØ	specific rate constants of the reactions, kg feed/(kg cat.)(h)
FMCØ	product of mass flow rate and specific heat, kcal/K
DCOH	heat generated per kg of catalyst, kcal
RHOF	density of the mixture, kg/m^3
TBPP	mid boiling point of the components, ^{o}C

SUMFØ	mass flow rate of the mixture, kg/h
PT	average reactor pressure, atm
T	temperature at the exit of the bed, K
HRT1	heat released during each reaction, kcal/ kg reactant
SG1	specific gravity of the components
WH1	mass flow rate of hydrogen, kg/h
CPH1	heat capacity of hydrogen, kcal/(kg)(K)
R1	carbon-to-hydrogen ratio
TC2	critical temperature of the components, K
VC2	critical volume of the components, cm^3/gmole
AMOL	molecular weight of the components
OMEGA	acentric factor of the components
PC2	critical pressure of the components, atm
TRW	mass of liquid reactant per unit mass of product for each reaction, kg
HW	mass of hydrogen required per unit mass of product for each reaction, kg
RNTH	enthalpy of the liquid reactant at standard conditions for each reaction, kcal/kg
ICON	=1 if temperature is to be printed at every step, otherwise 2
X	=Ø, mass fraction of catalyst at the inlet of the bed
X1	=1, mass fraction of catalyst at the exit of the bed
W1	total mass of the catalyst per bed
H	step size for integration
D6,QQ,Q, AA,B,C	parameters in Runge-Kutta-Gill method
FMF1	mol fraction of the components in the reaction mixture
ENTH1	enthalpy of the liquid mixture at reaction temperature,

kcal/kg

P   product distribution based on unit mass of the product

RENTH   enthalpy of the liquid reactant at reaction temperature for each reaction, kcal/kg

DC   change in the mass of the reactants due to reaction

DCM $= dC/dX$

DCOH   heat generated due to reaction , kcal/kg

D,D1,D2
D3,DD,DD1   parameters in Runge-Kutta-Gill method

FMCØ   product of mass flow rate and specific heat of the reaction mixture plus product of mass flow rate and specific heat of the gaseous reactant, kcal/(K)(h)

DCE $=dT/dX$

SUBROUTINE KINDAT

TEMP2   reaction temperature, K

TBP   mid boiling point of the components, $^{\circ}$C

AK1   specific rate constant of all the reactions,

           kg reactant/(kg catalyst)(h)

N   total number of the components

M1   component number of the lightest component undergoing cracking

X   Arrhenius expression for a component having a boiling point of 365 $^{\circ}$C(638 K)

AKT1   relative rate constant at reaction temperature for all the reactions

AK1   specific rate constants for all the reactions

SUBROUTINE PROP:

TB1   mid-boiling point of the components, $^{\circ}$C

SG1   specific gravity of the components

N	number of components
TC1	critical temperature of the components, K
PC1	critical pressure of the components, atm
VC1	critical volume of the components, cm^3/gmole
AMW	molecular weight of the components
OMEGA	acentric factor of the components
TB2	mid-boiling point in degree Rankine or Kelvine
TBR1	reduced normal boiling point
A1,A2	the numerator and denominator terms in the Lee-Kesler's correlation for calculating the acentric factor
ZC	critical compressibility factor of the components

SUBROUTINE MIXCRI:

CCØ	mass fraction of the components based on the mass of the liquid reaction mixture
TCM	mean critical temperature of the liquid reaction mixture, K
AMW1	molecular weight of the components
FMF	mole fraction of the components based on the total moles of liquid reactant
AM	required for conversion of mass fraction to mole fraction
VCM	mixture critical volume calculated by using mixing rule, cm^3/gmole

SUBROUTINE HTRXN:

M	component number of the lightest component undergoing cracking
N	total number of components

R1   carbon-to-hydrogen ratio of the components

P   product distribution based on unit mass of the product
            for all the reactions

HRT1   heat of reaction at standard conditions, kcal/kg
            reactant

TRW   mass of the liquid reactant per unit mass of product
            for all the reactions

HW   mass of hydrogen required per unit mass of product for
            all the reactions

TBPP   mid-boiling point of the components, ^{o}C

L   =1 for stage 1 and equal to 2 for stage 2 if heat of
            reaction is different for both the reactor

C   mass of carbon present in the product per unit mass of
            product

SUBROUTINE PRODIS

B,C   parameters in Stangeland's model for predicting   the
            hydrocracker yield

TB1   mid-boiling point of the components, ^{o}C

P   product distribution per unit mass of the product for
            all the reactions

PY   cumulative product distribution till the ith component

PY2   cumulative product distribution till (i-1)th component

SUBROUTINE ENTHL:

TC   critical temperature of the components, K

PC   critical pressure of the components, atm

OMEGA   acentric factor of the components

PT   pressure at which the enthalpy is to be calculated, atm

T   temperature at which enthalpy is to be calculated, K

Y   mole fraction of the components based on the total

moles of liquid reaction mixture

ENTH   enthalpy of the liquid reaction mixture, kcal

SG1   specific gravity of the components

TBPP   mid-boiling point of the components, $^{\circ}C$

N   total number of the components

AMW   molecular weight of the components

HILN,PHIL1 partial fugacity co-efficient

PHI,PHI1 fugacity co-efficient

HEX   excess enthalpy , kcal/kg

R   universal gas constant, kcal/(kmol)(K)

AVWM   average molecular weight of the liquid reaction mixture

TR   temperature in R

TF   temperature in $^{\circ}F$

HIDL   enthalpy of an ideal gas mixture at reaction temperature, kcal/kg

HID   enthalpy of an ideal gas at reaction temperature, kcal/kg

SUBROUTINE COENTH:

TC2   critical temperature of the components, K

PC2   critical pressure of the components, atm

OMEGA   acentric factor of the components

PT   reaction pressure, atm

T   reaction temperature, K

RENTH   enthalpy of the products minus enthalpy of the reactants, kcal/kg

SG1   specific gravity of the components

TBPP   mid-boiling point of the components, $^{\circ}C$

N   total number of components

AMOL   molecular weight of the components

TRW   mass of liquid reactant per unit mass of the product for all the reactions

HW   mass of hydrogen required per unit mass of the product for all the reactions

P   product distribution per unit mass of the product for all the reactions

R   universal gas constant, kcal/kmol K

Y   mole fraction of the components based on total moles of liquid reactants

HILN   partial fugacity co-efficient of the components
PHIL

PHI,PHI1   fugacity coefficient of the components

TR   temperature in Rankine

TF   temperature in ^{O}F

HEX   excess enthalpy of the components, kcal/kg

ENTH   enthalpy of the components, kcal/kg

HC   enthalpy of unit mass of hydrogen at reaction temperature and pressure, kcal

SUBROUTINE PHILN:

TC   critical temperature of the components, K

PC   critical pressure of the components, atm

OMEGA   acentric factor of the components

PT   reaction pressure, atm

T   reaction temperature, K

Y   mole fraction of the components based on total moles of liquid reactants

HILN   partial fugacity co-efficient of the components

PHI   fugacity co-efficient of ther components

N	total number of components
L	=1 for calculating fugacity co-efficient
	=2 for calculating partial fugacity co-efficient
TR	reduced temperature
A1,B1,ALFA	various parameters in Peng-Robinson's equation of
ALFAA,A,B	state
ALF,YALF	
Z	compressibility factor

SUBROUTINE CUBEQ:

AØ,BØ	parameters in Peng-Robinson's equation of state
B1,C1,D1	co-efficients of Peng-Robinson's cubic equation of state
P1,P2	parameters in the analytical method for finding the
Q1,Q2	roots of a cubic equation
R1,PHI	
ZØ	compressibility factor

SUBROUTINE STENTH:

SG1	specific gravity of the components
T	temperature at which enthalpy is to be calculated, $^{\circ}C$
TB	mid boiling point of the compoents, $^{\circ}C$
RNTH	enthalpy of the products minus the reactants, kcal/kg
TRW	mass of liquid reactant per unit mass of product
HW	mass of hydrogen required per unit mass of product
AMOL	molecular weight of the components
P	product distribution per unit mass of product for all the reactions
N	total number of components
TBK	mid-boiling point in Kelvine

ENT	enthalpy of the components, kcal/kg
CPH	heat capacity of hydrogen at temperature T, kcal/kg K
HEN	enthalpy of unit mass of hydrogen at T, kcal

4) DIMENSION REQUIREMENTS :

The DIMENSION statement in the MAIN program as well as in the subroutines should be modified according to the requirements of a specific problem. N refers to the number of pseudo- components in the feed.

MAIN:

```
DIMENSION  V(N),SG(N),FV(N),FM(N),P(N,N),CC(N),TB(N),CCN(N),AK(N)
           API(N),R1(N),FM2(N),CC2(N),FM3(N),CC3(N),FM4(N)
           AMOL(N),HRT(N),TC(N),TC(N),PC(N),VC(N),OMEGA(N),TRW(N)
           HW(N),RNTH(N),FN(N),CN(N)
```

SUBROUTINE DGIL

```
DIMENSION  CCØ(N),Q(N),AA(4),B(4),C(4),DC(N),FMØ(N),AKØ(N)
           TBPP(N),P(N,N),DCM(N),AMOL(N),HRT1(N),DE(N),R1(N)
           SG1(N),TC2(N),VC2(N),V2(N),CD(N),PC2(N),OMEGA(N)
           FMF1(N),TRW(N),HW(N),RENTH(N),RENTH(N),RNTH(N)
```

SUBROUTINE KINDAT

```
DIMENSION  TBP(N),AKT1(N),AK1(N)
```

SUBROUTINE PROP

```
DIMENSION  AMW(N),SG1(N),TB1(N),TC1(N),PC1(N),VC1(N),TBK(N),R1(N)
           TB2(N),OMEGA(N),TBR1(N),ZC(N)
```

SUBROUTINE MIXCRI

```
DIMENSION  TC1(N),VC1(N),FMF(N),CCØ(N),AM(N),SG1(N),AMW1(N)
```

SUBROUTINE HTRXN

```
DIMENSION  R1(N),C(N),HW(N),P(N,N),TRW(N),HRT1(N)
```

SUBROUTINE PRODIS:

DIMENSION TB1(N),PY(N,N),P(N,N),Y(N)

SUBROUTINE ENTHL:

DIMENSION TC(N),PC(N),OMEGA(N),Y(N),SG1(N),HILN(N+1),PHIL1(N+1)
          PHI(N+1),PHI1(N+1),AMW(N),AK(N),HID(N)

SUBROUTINE COENTH:

DIMENSION TC2(N),PC2(N),OMEGA(N),Y(N),HILN(N+1),PHI(N+1)
          PHI1(N+1),PHIL1(N+1),HIDL(N),HEX(N),RENTH(N),ENTH(N)
          AMOL(N),TRW(N),HW(N),SG1(N),P(N,N)

SUBROUTINE PHILN:

DIMENSION TC(N),PC(N),OMEGA(N),Y(N),A(N+1),B(N+1),Z(N+1,3)
          ALFAA(N),HILN(N+1),PHI(N+1),TR(N),YALF(N),A1(N+1)
          B1(N)

SUBROUTINE CUBEQ:

DIMENSION AØ(N+1),BØ(N+1),ZØ(N+1,3)

SUBROUTINE STENTH:

DIMENSION TB(N),RNTH(N),TRW(N),HW(N),ENT(N),AMOL(N),P(N,N)

5) INPUTS TO BE SUPPLIED BY THE USER

1. Number of components

2. Component number of the lightest component undergoing cracking

3. Number of steps for integration

4. Mid-boiling point of the fraction, $^{\circ}C$

5. API gravity of the components

6. Carbon-to-hydrogen ratio of the components

7. Volumetric composition of the components in the feed, %

8. Parameter 'B' and 'C' for Stangeland's model

9. Bulk density of the catalyst bed, kg/m^3

10. Total volumetric feed flow rate to the reactor, m^3/h

11. Hydrogen flow rate to the reactor, Nm^3/h

12. Inlet temperature of the reactor, K

13. Density of hydrogen at NTP, kg/Nm^3

14. Volume of catalyst per bed and number of beds, m^3

15. Average reactor pressure, atm

16. Heat capacity of hydrogen at reaction temperature and pressure, kcal/(kg)(K)

17. Hydrogen quenching rate between the beds, Nm^3/h

18. Temperature of the quenching stream, K

19. Feed flow rate and hydrogen flow rate to the second stage, m^3/h and Nm^3/h respectively

20. Inlet reactor temperature of the second stage

21. Volume of catalyst per bed in the second stage and number of beds, m^3

22. Average reactor pressure of the second stage, atm

23. Hydrogen quenching rate between the beds, Nm^3/h

24. Temperature of the quenching stream, K

25. Maximum number of iterations and convergence criteria ie. the minimum difference between two consecutive iterations

```
C*******************************************************************
C PROGRAM FOR PREDICTING HYDROCRACKER YIELD USING STANGELAND MODEL
C*******************************************************************
          DIMENSION V(25),SG(25),FV(25),FM(25),P(25,25),CC(25),TB(25)
         1,AKT(25),DC(25),CCN(25),AK(25),API(25),R1(25)
         1,FM2(25),CC2(25),FM3(25),CC3(25),AMOL(25),HRT(25
         1),TC(25),PC(25),VC(25),OMEGA(25),TRW(25),HW(25),RNTH(25)
         1,CN(25),FN(25)
C*******************************************************************
C         N=NO. OF PSEUDO-COMPONENTS
C         M1=COMPONENT NO.OF THE LIGHTEST COMPONENT UNDERGOING CRACKING
C         N2=NO. OF STEPS  USED FOR SOLVING THE DIFFRENTIAL EQUATIONS
C         USING RUNGE-KUTTA-GILL METHOD.
C*******************************************************************
          N=23
          M1=6
          N2=25
          READ (21,*) (TB(I),I=1,N)
          READ(21,*) (API(I),I=1,N)
          READ(21,*) (R1(I),I=1,N)
          READ(21,*)(V(I),I=1,N)
          B=.7
          C1=.37
          DO 23 I=1,N
          SG(I)=141.5/(API(I)+131.5)
    23    CONTINUE
          CALL PROP(TB,SG,N,TC,PC,VC,AMOL,OMEGA)
C         DO 3 I=1,23
C         WRITE(62,1)
C    1    FORMAT(4X,'TC K',6X,'PC ATM',6X,'AMOL',6X,'OMEGA')
C         WRITE(62,2) TC(I),PC(I),AMOL(I),OMEGA(I)
C    2    FORMAT(2X,F6.2,6X,F6.2,6X,F7.2,6X,F6.4)
C    3    CONTINUE
          CALL PRODIS(B,C1,TB,P,N,M1)
C         WRITE(62,602)((P(I,J),J=1,N-2),I=1,N)
C  602    FORMAT(2X,21(F4.3,1X)/2X)
C         RHOB=BED DENSITY
          RHOB=741.
    52    SUMF=0.
          WHYI=0.
          DO 40 I=1,N
          FT=227.
          FV(I)=V(I)*FT/100.
          FM(I)=FV(I)*SG(I)*1000.
          WHYI=WHYI+FM(I)/(R1(I)+1.)
          SUMF=SUMF+FM(I)
    40    CONTINUE
          RHOF=SUMF/(FT*1000.)
          DO 50 I=1,N
          CC(I)=FM(I)/SUMF
    50    CONTINUE
          CALL HTRXN(M1,N,SG,R1,P,HRT,TRW,HW,TBP,1)
          WRITE(62,*) HRT
```

```
C*******************************************************************
C          TEMP=INLET TEMP. OF THE REACTOR IN 'K'
C          STEMP=REFERENCE TEMPERATURE=25 DEG. CENTIGRADE
C          HPM=HYDROGEN PER M**3 OF FEED
C          RHOH=DENSITY OF HYDROGEN AT NTP
C          VCAT=VOLUME OF CATALYST PER BED
C          CPH=SP. HEAT OF HYDROGEN AT REACTION TEMP. AND PRESSURE
C          PT=AVERAGE PRESSURE OF THE REACTOR
C          QUENCH=VOLUME OF HYDROGEN USED FOR COOLING FOR EACH BED
C          N1=NO. OF BEDS
C*******************************************************************
           TEMP=672.
           STEMP=25.
           CALL STENTH(SG,STEMP,TB,RNTH,TRW,HW,AMOL,P,N)
           A2=.9906
           CALL KINDAT(TEMP,TB,AK,N,A2,M1)
           WRITE(23,*) AK
           HPM=800.
           VH=FT*HPM
           N1=4
           RHOH=.08995
           VCAT=37.3
           CPH=3.5
           PT=176.
           QUENCH=43583.
           DO 69 I1=1,N1
           WH=VH*RHOH
           ICON=1
           CALL DGIL(CC,M1,N,N2,VCAT,FM,TEMP,AK,FMCP,RHOF,RHOB,TB
          1,SUMF,P,T2,HRT,SG,WH,CPH,R1,TC,VC,AMOL,OMEGA,PC,TRW,
          1HW,RNTH,A2,PT,ICON)
           WHYE=0.
           DO 51 I=1,N
           WHYE=WHYE+FM(I)/(R1(I)+1.)
   51      CONTINUE
           WRITE(62,*)TEMP,T2,FMCP
           VH=VH+QUENCH
           IF(I1.EQ.4)GO TO 69
           TH2=361.
           FHCP=CPH*QUENCH*RHOH
           TEMP=(FMCP*T2+FHCP*TH2)/(FMCP+FHCP)
           WRITE(62,*)TEMP
   69      CONTINUE
           WRITE(62,65)
   65      FORMAT(///)
           HCON=WHYE-WHYI
           WRITE(62,68) A,B,C1,A2,HCON
   68      FORMAT (3X,'A=',F5.2,'B=',F5.2,'C=',F5.2,'K=',F5.3,'HCON=',
          1F9.2)
           WRITE(62,401)
  401      FORMAT(1X,//6X,'FM',9X,'CC',9X,'I',8X,'SUMF')
           DO 42 I=1,N
           WRITE(62,402) FM(I),CC(I),I,SUMF,TEMP,T2
   42      CONTINUE
  402      FORMAT(1X,1X,F10.2,4X,F7.5,3X,I3,3X,F10.2,3X,F7.2,3X,F7.2)
           REC=0.
           RECC=0.
```

```
          HSD=Ø.
          HSDC=Ø.
          ATF=Ø.
          ATFC=Ø.
          HNH=Ø.
          HNHC=Ø.
          C4L=FM(1)
          C4LC=CC(1)
          DO 43 I=16,N
          IF (I.EQ.16) REC=REC+FM(I)*20./25.
          IF(I.EQ.16)RECC=RECC+CC(I)*20./25.
          IF(I.EQ.16) GO TO 43
          REC=REC+FM(I)
          RECC=RECC+CC(I)
   43     CONTINUE
          DO 45 I=11,16
          IF(I.EQ.11)HSD=HSD+FM(I)*15./25.
          IF(I.EQ.11)HSDC=HSDC+CC(I)*15./25.
          IF(I.EQ.16)HSD=HSD+FM(I)*5./25.
          IF(I.EQ.16)HSDC=HSDC+CC(I)*5./25.
          IF(I.EQ.11.OR.I.EQ.16) GO TO 45
          HSD=HSD+FM(I)
          HSDC=HSDC+CC(I)
   45     CONTINUE
          DO 47 I=7,11
          IF(I.EQ.11)ATF=ATF+FM(I)*1Ø./25.
          IF(I.EQ.11)ATFC=ATFC+CC(I)*1Ø./25.
          IF(I.EQ.11)GO TO 47
          ATF=ATF+FM(I)
          ATFC=ATFC+CC(I)
   47     CONTINUE
          DO 49 I=2,6
          HNH=HNH+FM(I)
          HNHC=HNHC+CC(I)
   49     CONTINUE
          WRITE(62,95) REC,HSD,ATF
   95     FORMAT(1X,´REC=´,F10.3,´HSD=´,F1Ø.3,1X,´ATF=´,F1Ø.3)
          WRITE(62,96) HNH,C4L
   96     FORMAT(2X,´HNH=´,F1Ø.3,1X,´C4L=´,F1Ø.3)
          WRITE(62,98) RECC,HSDC,ATFC,HNHC,C4LC
   98     FORMAT(2X,´REC CONC=´,F8.6,1X,´HSDC=´,F8.6,1X,´ATFC=´,F8.6,
    2     1X,´HNHC=´,F8.6,1X,´C4 AND LOWER CONC=´,F8.6)
          SUMF2=Ø.
          DO 72 I=16,N
          IF(I.EQ.16)FM2(I)=FM(I)*2Ø./25.
          IF(I.EQ.16)GO TO 2Ø1
          FM2(I)=FM(I)
  2Ø1     SUMF2=SUMF2+FM2(I)
   72     CONTINUE
          RHO2=Ø.
          DO 73 I=16,N
          CC2(I)=FM2(I)/SUMF2
          RHO2=RHO2+CC2(I)*SG(I)
   73     CONTINUE
```

```
C*****************************************************************************
C          RECYCLE AND PRODUCT DISTRIBUTION CALCULATIONS FOR THE SECOND
C          STAGE
C          FTS=VOLUMETRIC FEED RATE TO THE SECOND STAGE
C          TEMP=INLET TEMP. OF THE SECOND STAGE REACTOR
C          TH2=TEMP.OF THE HYDROGEN QUENCH
C*****************************************************************************
           RHO2=RHO2*1000.
           FTS=202.
           SUM2=FTS*RHO2
           NR=0
    103    WHYI=0.
           NR=NR+1
           DO 81 I=1,N
           WHYI=WHYI+SUM2*CC2(I)/(R1(I)+1.)
     81    CONTINUE
           TEMP=644.
           VH=FTS*HPM
           A2=.7844
           ICON=2
           VCAT=50.
           PT=172.5
           QUENCH=8400.
           N1=3
           DO 71 I1=1,N1
           WH=VH*RHOH
           CALL DGIL(CC2,M1,N,N2,VCAT,FM3,TEMP,AK,FMCP,RHOF,RHOB,TB
          1,SUM2,P,T2,HRT,SG,WH,CPH,R1,TC,VC,AMOL,OMEGA,PC,TRW,HW
          1,RNTH,A2,PT,ICON)
           WHYE=0.
           DO 83 I=1,N
           WHYE=WHYE+ FM3(I)/(R1(I)+1.)
     83    CONTINUE
           WRITE(62,*)TEMP,T2,FMCP
           VH=VH+QUENCH
           IF(I1.EQ.3)GO TO 71
           TH2=354.
           FHCP1=QUENCH*RHOH*CPH
           TEMP=(FMCP*T2+FHCP1*TH2)/(FMCP+FHCP1)
     71    CONTINUE
           SUMF3=0.
           RHO3=0.
           DO 74 I=16,N
           IF(I.EQ.16)SUMF3=SUMF3+FM3(I)*20./25.
           IF(I.EQ.16)RHO3=RHO3+SG(I)*FM3(I)*20./25.
           IF(I.EQ.16)GOTO 74
           SUMF3=SUMF3+FM3(I)
           RHO3=RHO3+SG(I)*FM3(I)
     74    CONTINUE
           RHO3=RHO3*1000./SUMF3
           SUM=SUMF3+SUMF2
           IF(ABS(SUM-COM).LE.40.) ICON=1
           IF(ABS(SUM-COM).LE.10) GO TO 78
           SUM2=FTS*(RHO3*SUMF3+RHO2*SUMF2)/SUM
           WRITE(62,101)SUM,COM,NR
    101    FORMAT(3X,'SUM=',F10.3,2X,'COM=',F10.3,3X,'NR=',I3)
           COM=SUM
```

```
          DO 82 I=16,N
          IF(I.EQ.16) CN(I)=FM3(I)*20./(SUMF3*25.)
          IF(I.EQ.16)GO TO 803
          CN(I)=FM3(I)/SUMF3
803       FN(I)=CN(I)*(SUM2-SUMF2)
 82       CONTINUE
          DO 75 I=1,N
          CC2(I)=(FM2(I)+FN(I))/SUM2
          IF(I.LT.16) CC2(I)=0.
 75       CONTINUE
          IF(NR.GE.10) GO TO 78
          GO TO 103
 78       WRITE (62,612) SUMF3,NR,TEMP
612       FORMAT (/4X, 'SUMF3=',F8.1,2X,'NR=',I3,2X,'TEMP=',F6.2,/)
          WRITE (62,614)
614       FORMAT (/11X,'FM3',9X,'CC2',10X,'I',/)
          DO 86 I=1,N
          WRITE(62,613) FM3(I),CC2(I), I
613       FORMAT (/8X,F8.1,5X, F8.5,5X, I3)
 86       CONTINUE
          REC1=0.
          REC1C=0.
          HSD1=0.
          HSD1C=0.
          ATF1=0.
          ATF1C=0.
          HNH1=0.
          HNH1C=0.
          C4L1=FM3(1)
          C4L1C=CC2(1)
          DO 53 I=16,N
          IF(I.EQ.16)REC1=REC1+FM3(I)*20./25.
          IF(I.EQ.16)REC1C=REC1C+CC2(I)*20./25.
          IF(I.EQ.16)GO TO 53
          REC1=REC1+FM3(I)
          REC1C=REC1C+CC2(I)
 53       CONTINUE
          DO 55 I=11,16
          IF(I.EQ.11) HSD1=HSD1+FM3(I)*15./25.
          IF(I.EQ.11)HSD1C=HSD1C+CC2(I)*15./25.
          IF(I.EQ.16)HSD1=HSD1+FM3(I)*5./25.
          IF(I.EQ.16)HSD1C=HSD1C+CC2(I)*5./25.
          IF(I.EQ.11.OR.I.EQ.16) GO TO 55
          HSD1=HSD1+FM3(I)
          HSD1C=HSD1C+CC2(I)
 55       CONTINUE
          DO 57 I=7,11
          IF(I.EQ.11) ATF1=ATF1+FM3(I)*10./25.
          IF(I.EQ.11) ATF1C=ATF1C+CC2(I)*10./25.
          IF(I.EQ.11)GO TO 57
          ATF1=ATF1+FM3(I)
          ATF1C=ATF1C+CC2(I)
 57       CONTINUE
          DO 59 I=2,6
          HNH1=HNH1+FM3(I)
          HNH1C=HNH1C+CC2(I)
 59       CONTINUE
```

```
          WRITE(62,105) REC1,HSD1,ATF1
105         FORMAT(//1X,'REC1=',F10.3,'HSD1=',F10.3,1X,'ATF1=',F10.3)
          WRITE(62,106) HNH1,C4L1
106          FORMAT(//2X,'HNH1=',F10.3,1X,'C4L1=',F10.3)
          WRITE(62,108) REC1C,HSD1C,ATF1C,HNH1C,C4L1C
108       FORMAT(//2X,'REC1 CONC=',F8.6,1X,'HSD1C=',F8.6,1X,'ATF1C=',F8.6,
     2    1X,'HNH1C=',F8.6,1X,'C4 AND LOWER CONC=',F8.6)
          RECT=REC+REC1
          HSDT=HSD+HSD1
          ATFT=ATF+ATF1
          HNHT=HNH+HNH1
          C4LT=C4L+C4L1
          TOT=HSDT+ATFT+HNHT+C4LT
          RECTC=RECT/TOT
          HSDTC=HSDT/TOT
          HNHTC=HNHT/TOT
          ATFTC=ATFT/TOT
          C4LTC=C4LT/TOT
          WRITE(62,95) RECT,HSDT,ATFT
          WRITE(62,96)HNHT,C4LT
          WRITE(62,98) RECTC,HSDTC,ATFTC,HNHTC,C4LTC
          HCON=WHYE-WHYI
          WRITE(62,99)HCON
99        FORMAT(4X,'HCON=',F10.2)
300       STOP
          END

C***********************************************************************
C         THIS SUBROUTINE USES THE RUNGE-KUTTA-GILL METHOD FOR
C         DETERMINING THE SOLUTION OF THE MASS AND ENERGY BALANCE
C         DIFFERENTIAL EQUATIONS
C***********************************************************************
          SUBROUTINE DGIL(CC0,M1,N,N2,BV,FM0,TEMP1,AK0,FMC0,RHOF,RHOB
     1    TBPP,SUMF0,P,T,HRT1,SG1,WH1,CPH1,R1,TC2,VC2,AMOL,OMEGA,
     1PC2,TRW,HW,RNTH,A2,PT,ICON)
          DIMENSION CC0(25),Q(25),AA(4),B(4),C(4),DC(25),FM0(25),AK0(25)
     1    ,TBPP(25),P(25,25),DCM(25),AMOL(25),HRT1(25),R1(25),
     1SG1(25),TC2(25),VC2(25),PC2(25)
     1,OMEGA(25),FMF(25),FMF1(25),TRW(25),HW(25),RENTH(25),RNTH(25)
          X=0.
          X1=1.
          N1=1
          W1=RHOB*BV
          H=(X1-X)/FLOAT(N2)
          D6=H*.5
          X=X+D6
          QQ=0.
          DO 1 I=1,N
1         Q(I)=0.
          AA(1)=.5
          B(1)=2.
          C(1)=.5
          AA(2)=1.-SQRT(.5)
          B(2)=1.
          C(2)=AA(2)
          AA(3)=1.+SQRT(.5)
          B(3)=1.
```

```
         C(3)=AA(3)
         AA(4)=1./6.
         B(4)=2.
         C(4)=.5
         L1=1
         CALL MIXCRI(TC2,VC2,SG1,CCØ,TCM1,N,AMOL,FMF1)
         CALL ENTHL(TC2,PC2,OMEGA,PT,TEMP1,FMF1,ENTH1,SG1,TBPP,N,AMOL
        1,L1,CCØ)
         CPM=ENTH1/(TEMP1-273.)
   4     CALL KINDAT(TEMP1,TBPP,AKØ,N,A2,M1)
         DO 3 J=1,4
         CALL COENTH(TC2,PC2,OMEGA,PT,TEMP1,RENTH,SG1,TBPP,N,AMOL,TRW,
        1HW,P,L1)
C        WRITE(62,21)(RENTH(I),I=1,N)
  21     FORMAT(///3X,4F10.2)
         DCOH=Ø.
         DO 70 I=1,N
         DC(I)=Ø.
         IF(I.LT.6)GO TO 81
         DC(I)=-AKØ(I)*CCØ(I)
         IF(I.GE.22) GO TO 90
         K=I+2
  81     IF(I.EQ.5)K=7
         IF(I.LT.5)K=6
         DO 60 J1=K,23
         DC(I)=(DC(I)+AKØ(J1)*P(J1,I)*CCØ(J1))
  60     CONTINUE
  90     DCM(I)=DC(I)*W1/SUMFØ
         DCOH=DCOH-((HRT1(I)+(RENTH(I)-RNTH(I)))*AKØ(I)*CCØ(I))
  70     CONTINUE
         DO 12 I=1,N
         D=AA(J)*(DCM(I)-B(J)*Q(I))
         D1=H*D
         CCØ(I)=CCØ(I)+D1
         D2=D*3.
         D3=C(J)*DCM(I)
         D2=D2-D3
         Q(I)=Q(I)+D2
  12     CONTINUE
         FMCØ=(WH1*CPH1)+SUMFØ*CPM
         DCE=DCOH*W1/FMCØ
         DD=AA(J)*(DCE-B(J)*QQ)
         DD1=H*DD
         TEMP1=TEMP1+DD1
         DD2=DD*3.
         DD3=C(J)*DCE
         DD2=DD2-DD3
         QQ=QQ+DD2
         IF(J.GT.1) GO TO 2
         GO TO 3
   2     IF(J.GT.2) GO TO 3
         X=X+D6
   3     CONTINUE
         IF(ICON.GT.1)GO TO 43
         WRITE(62,42) N1,X,TEMP1
  42     FORMAT(4X,'N1=',I3,3X,'X=',F5.2,3X,'TEMP=',F7.2)
  43     IF(N1.EQ.N2)GO TO 5
```

```
            N1=N1+1
            IF(X.GT.X1)GO TO 5
            X=X+D6
      23    FORMAT(///3X,4(F8.5,2X))
            GO TO 4
       5    T=TEMP1
            DO 41 I=1,N
            FMØ(I)=CCØ(I)*SUMFØ
      41    CONTINUE
            RETURN
            END


C*****************************************************************
C         THIS SUBROUTINE CALCULATES THE FIRST-ORDER RATE CONSTANTS
C         FOR ALL THE COMPONENTS USING AN EMPERICAL CORRELATION  GIVEN
C         AS A FUNCTION OF TRUE BOILING POINT
C*****************************************************************
            SUBROUTINE KINDAT(TEMP2,TBP,AK1,N,A2,M1)
            DIMENSION TBP(25),AKT1(25),AK1(25),T(25)
            X=A2*(10.**7)*(EXP(-21100./(1.987*TEMP2)))
            DO 10 I=M1,N
            AKT1(I)=.494+.52E-02*TBP(I)-2.185E-05*TBP(I)**2+.312E-07*TBP(I)
           1**3
            AK1(I)=AKT1(I)*X
      10    CONTINUE
            RETURN
            END


C*****************************************************************
C         THIS SUBROUTINE CALCULATES THE CRITICAL PROPERTIES OF ALL THE
C         COMPONENTS AS WELL AS THE MOLECULAR WEIGHT AND ACCENTRIC
C         FACTOR USING LEE-KESLER'S CORRELATIONS
C*****************************************************************
            SUBROUTINE PROP(TB1,SG1,N,TC1,PC1,VC1,AMW,OMEGA)
            DIMENSION AMW(25),SG1(25),TB1(25),TC1(25),PC1(25),VC1(25),
           1TBK(25),R1(25),TB2(25),OMEGA(25),TBR1(25),ZC(25)
            DO 10 I=1,N
            TB2(I)=(TB1(I)*9./5.)+492.
            AMW(I)=-12272.6+9486.4*SG1(I)+(4.6523-3.3287*SG1(I))*TB2(I)+(1.-
           1.77084*SG1(I)-.02058*(SG1(I)**2))*(1.3437-720.79/TB2(I))*
           1(10.**7)/TB2(I)+(1.-.80882*SG1(I)+.02226*(SG1(I)**2))*(1.8828-
           1181.98/TB2(I))*(10.**12)/(TB2(I)**3)
            TC1(I)=341.7+811*SG1(I)+(.4244+.1174*SG1(I))*TB2(I)+(.4669
           1-3.2623*SG1(I))*(10.**5)/TB2(I)
            PC1(I)=EXP(8.3634-.0566/SG1(I)-(.24244+2.2898/SG1(I)+
           1.11857/(SG1(I)**2))*(10.**-3)*TB2(I)+(1.4685+3.648/SG1(I)
           1+.47227/(SG1(I)**2))*(10.**-7)*(TB2(I)**2)-(.42019+1.6977/
           1(SG1(I)**2))*(10.**-10)*(TB2(I)**3))
            TB2(I)=TB1(I)+273.
            TBR1(I)=TB2(I)/((TC1(I)-492.)*5./9.+273.)
            PC1(I)=PC1(I)/14.69
            A1=ALOG(1./(PC1(I)))-5.92714+(6.09648/TBR1(I))+1.28862*ALOG(TBR1
           1(I))-(.169547*(TBR1(I)**6))
            A2=15.2518-(15.6875/TBR1(I))-(13.4721*ALOG(TBR1(I)))+(.43577*(TB
           1R1(I)**6))
            OMEGA(I)=A1/A2
            TC1(I)=(TC1(I)-492.)*5./9.+273.
```

```
              R=82.06
              ZC(I)=.2905-(.085*OMEGA(I))
              VC1(I)=ZC(I)*R*TC1(I)/PC1(I)
      10      CONTINUE
              RETURN
              END


C*******************************************************************
C         THIS SUBROUTINE CALCULATES THE CRITICAL PRORERTIES OF A
C         MULTI-COMPONENT MIXTURE
C*******************************************************************

              SUBROUTINE MIXCRI(TC1,VC1,SG1,CC0,TCM,N,AMW1,FMF)
              DIMENSION TC1(25),VC1(25),FMF(25),CC0(25),AM(25),PHII
              1(25),TTC(25,25),SG1(25),AMW1(25)
              SUM=0.
              DO 40 I=1,N
              AM(I)=CC0(I)/AMW1(I)
              SUM=SUM+AM(I)
      40      CONTINUE
              SUM1=0.
              DO 50 I=1,N
              FMF(I)=AM(I)/SUM
              SUM1=SUM1+FMF(I)*VC1(I)
      50      CONTINUE
              VCM=0.
              DO 60 I=1,N
              DO 60 J=1,N
              VCM=VCM+FMF(I)*FMF(J)*(VC1(I)**(1./3.)+VC1(J)**(1./3.))**3
      60      CONTINUE
              VCM=VCM/8.
              TCM=0.
              DO 70 I=1,N
              DO 70 J=1,N
              TCM=TCM+FMF(I)*FMF(J)*(VC1(I)**(1./3.)+VC1(J)**(1./3.))**3
              1*(SQRT(TC1(I)*TC1(J)))
      70      CONTINUE
              TCM=TCM/(8.*VCM)
              RETURN
              END


C*******************************************************************
C         THIS SUBROUTINE CALCULATES THE STANDARD HEAT OF REACTION
C         IN KCALS/KG OF HYDROGEN CONSUMED AND IS BASED ON THE BOND TYPE
C*******************************************************************
              SUBROUTINE HTRXN(M,N,SG1,R1,P,HRT1,TRW,HW,TBPP,L)
              DIMENSION R1(25),SG1(25),API(25),C(25),HW(25),P(25,25),TRW(25),
              1HRT1(25),H(25),QU(25),A3(25),TBPP(25),AK(25)
              HC=-68317./2.
              DO 50 I=M,N
              C(I)=0.
              HW(I)=0.
              HRT1(I)=0.
              DO 60 J=1,I-2
              C(I)=C(I)+(R1(J)/(R1(J)+1.))*P(I,J)
              HW(I)=HW(I)+(1./(R1(J)+1.))*P(I,J)
      60      CONTINUE
              TRW(I)=C(I)*(1.+1./R1(I))
```

```
            HW(I)=HW(I)-C(I)/R1(I)
  90        CONTINUE
            HRT1(I)=-HW(I)*10000./(2.*TRW(I))
            IF(L.EQ.1) HRT1(I)=-HW(I)*10000./(2.*TRW(I))
  50        CONTINUE
            WRITE(62,70)
  70        FORMAT(3X,'HTREAC',3X,'TRW',5X,'HW',6X,'HC')
            DO 80 I=1,N
            WRITE(62,*) HRT1(I),TRW(I),HW(I),QU(I),A3(I)
  80        CONTINUE
 100        RETURN
            END


C*****************************************************************
C       THIS SUBROUTINE USES STANGELANDS MODEL FOR PREDICTING THE PRO
C       -DUCT DISTRIBUTION FOR HYDROCRACKING REACTIONS
C*****************************************************************
            SUBROUTINE PRODIS(B,C,TB1,P,N,M1)
            DIMENSION TB1(25),PY(25,25),P(25,25),Y(25)
            DO 20 I=M1,N
            P(I,1)=C*EXP(-.00693*(TB1(I)*9/5.+32.-261.5))
            PY2=0.
            DO 30 K=2,I-2
            Y(K)=(TB1(K)-2.5)/(TB1(I)-52.5)
            PY(I,K)=(Y(K)**2+B*(Y(K)**3-Y(K)**2))*(1.-P(I,1))
            P(I,K)=PY(I,K)-PY2
            PY2=PY(I,K)
  30        CONTINUE
  20        CONTINUE
            RETURN
            END


C*****************************************************************
C       THIS SUBROUTINE USES PENG-ROBINSON'S EQUATIONS OF STATE FOR
C       PREDICTING THE ENTHALPY OF A MULTI-COMPONENT MIXTURE
C*****************************************************************
            SUBROUTINE ENTHL(TC,PC,OMEGA,PT,T,Y,ENTH,SG1,TBPP,N,AMW,L1,CC)
            DIMENSION TC(25),PC(25),OMEGA(25),Y(25),SG1(25),TBPP(25),
           1HILN(26),PHIL1(26),PHI(26),PHI1(26),AMW(25),AK(25),HID(25)
           1,CF(25),CP(25),TBPR(25),CC(25)
            CALL PHILN(TC,PC,OMEGA,PT,T,Y,HILN,PHI,N,2,L1)
            CALL PHILN(TC,PC,OMEGA,PT,(T*1.0001),Y,PHIL1,PHI1,N,2,L1)
            HEX=0.
            DO 10 I=1,N
            HEX=HEX+((PHIL1(I)-HILN(I))*Y(I)/(.0001*T))
  10        CONTINUE
            R=1.987
            AVMW=0.
            DO 11 I=1,N
            AVMW=AVMW+(Y(I)*AMW(I))
  11        CONTINUE
            HEX=-R*(T**2)*HEX/AVMW
            TR=(T-273.)*9./5.+492.
            TF=(T-273.)*9./5.+32.
            HIDL=0.
            DO 20 I=1,N
```

```
      HID(I)=215.-87.*SG1(I)+(.415-.104*SG1(I))*TF+(.000310-.000078*SG
     11(I))*TF**2
      HIDL=HIDL+CC(I)*HID(I)*252./453.5
 20   CONTINUE
      ENTH=HEX+HIDL
      RETURN
      END


C**********************************************************************
C         THIS SUBROUTINE USES PENG-ROBINSON'S EQUATIONS OF STATE FOR
C         PREDICTING THE ENTHALPY DIFFERENCE BETWEEN THE PRODUCT AND
C         THE REACTANTS FOR ALL THE REACTIONS AT THE REACTION TEMPERATURE
C**********************************************************************
      SUBROUTINE COENTH(TC2,PC2,OMEGA,PT,T,RENTH,SG1,TBPP,N,AMOL,TRW,
     1HW,P,L1)
      DIMENSION TC2(25),PC2(25),OMEGA(25),Y(25),HILN(26),PHI(26),
     1PHI1(26),PHIL1(26),HIDL(25),HEX(25),RENTH(25),RNTH(25),ENTH(25)
     1,TBPP(25),AMOL(25),TRW(25),HW(25),SG1(25),AK(25),CF(25),CP(25),
     1P(25,25),TBPR(25)
      DO 102 I=1,N
      Y(I)=1.
 102  CONTINUE
      R=1.987
      CALL PHILN(TC2,PC2,OMEGA,PT,T,Y,HILN,PHI,N,1,L1)
      CALL PHILN(TC2,PC2,OMEGA,PT,(T*1.0001),Y,PHIL1,PHI1,N,1,L1)
      TR=(T-273.)*9./5.+492.
      TF=(T-273.)*9./5.+32.
      DO 100 I=1,N
      HEX(I)=(PHI1(I)-PHI(I))/(.0001*T*AMOL(I))
      HEX(I)=-R*(T**2)*HEX(I)
      HIDL(I)=(215.-87.*SG1(I)+(.415-.104*SG1(I))*TF+(.000310-.000078
     1*SG1(I))*TF**2)*252./453.5
      ENTH(I)=HEX(I)+HIDL(I)
 100  CONTINUE
      HC=3.58*(T-273.)
      DO 10 I=6,23
      RENTH(I)=-(TRW(I)*ENTH(I)+(HW(I)*HC))
      DO 60 J=1,I-2
      RENTH(I)=RENTH(I)+ENTH(J)*P(I,J)
 60   CONTINUE
      RENTH(I)=RENTH(I)/TRW(I)
 10   CONTINUE
      RETURN
      END


C**********************************************************************
C         THIS SUBROUTINE CALCULATES THE FUGACITY COEFFICIENT FOR A MIXTUR
C         -E AS WELL  AS FOR PURE COMPONENTS USING PENG-ROBINSON'S EQUATIO
C         -NS OF STATE
C**********************************************************************
      SUBROUTINE PHILN(TC,PC,OMEGA,PT,T,Y,HILN,PHI,N,L,L1)
      DIMENSION TC(25),PC(25),OMEGA(25),Y(25),A(26),B(26),Z(26,3)
     1,ALFAA(25),HILN(26),PHI(26),TR(25),YALF(25),A1(25),B1(25)
      DO 10 J=1,N
      TR(J)=T/TC(J)
      YALF(J)=0.
      R=.08205
```

```
          A1(J)=.45724*(R**2)*(TC(J)**2)/(PC(J))
          B1(J)=.07780*R*TC(J)/PC(J)
          ALFA=(1.+(.37464+(1.54226*OMEGA(J))-(.26992*(OMEGA(J)**2)))*(1.-
         1(TR(J)**.5)))**2
          ALFAA(J)=ALFA*A1(J)
          A(J)=ALFAA(J)*PT/((R**2)*(T**2))
          B(J)=B1(J)*PT/(R*T)
   10     CONTINUE
          IF(L.EQ.1)GO TO 70
          A(N+1)=0.
          B(N+1)=0.
          ALF=0.
          DO 20 J=1,N
          B(N+1)=B(N+1)+B(J)*Y(J)
          DO 30 I=1,N
          A(N+1)=A(N+1)+Y(I)*Y(J)*((A(J)*A(I))**.5)
          ALF=ALF+(Y(I)*Y(J))*SQRT(ALFAA(I)*ALFAA(J))
          YALF(J)=YALF(J)+Y(I)*SQRT(ALFAA(I)*ALFAA(J))
   30     CONTINUE
   20     CONTINUE
   70     CALL CUBEQ(A,B,N,Z,L,L1)
          IF(L.EQ.1)GO TO 80
          DO 40 I=1,N
          HILN(I)=(B(I)/B(N+1))*(Z(N+1,1)-1.)-(ALOG(Z(N+1,1)-B(N+1)))+(A(N
         1+1)/(4.828*B(N+1)))*(B(I)/B(N+1)-(2.*YALF(I)/ALF))*(ALOG((Z(N+1
         1,1)+2.414*B(N+1))/(Z(N+1,1)-.414*B(N+1))))
   40     CONTINUE
          GO TO 100
   80     DO 90 I=1,N
          PHI(I)=Z(I,1)-1.-ALOG(Z(I,1)-B(I))-(A(I)/(B(I)*4.828))*ALO
         1G((Z(I,1)+(2.414*B(I)))/(Z(I,1)-(.414*B(I))))
   90     CONTINUE
  100     RETURN
          END


C*********************************************************************
C       THIS SUBROUTINE CALCULATES THE THREE ROOTS OF A CUBIC EQUATION
C       ANALYTICALLY
C*********************************************************************
          SUBROUTINE CUBEQ(A0,B0,N0,Z0,L,L1)
          DIMENSION A0(26),B0(26),Z0(26,3)
          IF(L.EQ.1) K1=N0
          IF(L.EQ.2) K1=N0+1
          DO 10 I=1,K1
          B1=B0(I)-1
          C1=A0(I)-(3.*(B0(I)**2))-(2.*B0(I))
          D1=-((A0(I)*B0(I))-(B0(I)**2)-(B0(I)**3))
          P=(3.*C1-(B1**2))/3.
          P1=(P/3.)**3
          Q1=(27.*D1-(9.*B1*C1)+(2.*(B1**3)))/27.
          Q2=(Q1/2.)**2
          R1=(P/3.)**3+((Q1/2.)**2)
          IF(R1.GT.0.)GO TO 100
          PHI=ACOS(((((Q1**2)/4.)/(-((P**3)/27.)))**.5)
          IF(Q1.GT.0.)GO TO 12
          DO 50 K=1,3
          Z0(I,K)=2.*((-P/3.)**.5)*COS(PHI/3.+(22.*120.*(K-1)/(7.*180.)))
```

```
          1-(B1/3.)
   50     CONTINUE
          GO TO 90
   12     DO 13 K=1,3
          Z0(I,K)=(-2.*((-P/3.)**.5))*COS(PHI/3.+(22.*120.*(K-1)/(7.*180.)
          1))-(B1/3.)
   13     CONTINUE
          GO TO 90
  100     AM=-Q1/2.+SQRT(R1)
          AN=-Q1/2.-SQRT(R1)
          IF(AM.LT.0.)GO TO 150
          AMD=(AM**(1./3.))
          GO TO 160
  150     AMD=(-AM)**(1./3.)
          AMD=-AMD
  160     IF(AN.LT.0.)GO TO 170
          AND=AN**(1./3.)
          GO TO 180
  170     AND=(-AN)**(1./3.)
          AND=-AND
  180     Z0(I,1)=AMD+AND-(B1/3.)
   90     IF(L1.EQ.2) GO TO 20
          IJ=0
          DO 30 K=1,3
          IF(Z0(I,K).LE.0.) GO TO 30
          IJ=IJ+1
          IF(IJ.EQ.1) SMALL=Z0(I,K)
          IF(Z0(I,K).LT.SMALL) SMALL=Z0(I,K)
   30     CONTINUE
          Z0(I,1)=SMALL
          GO TO 10
   20     BIG=Z0(I,1)
          DO 40 K=1,3
          IF(Z0(I,K).GT.BIG)BIG=Z0(I,K)
   40     CONTINUE
          Z0(I,1)=BIG
   10     CONTINUE
  200     RETURN
          END

C***********************************************************************
C         THIS SUBROUTINE CALCULATES THE ENTHALPY DIFFERENCE BETWEEN THE
C         PRODUCTS AND THE REACTANTS FOR ALL THE REACTIONS AT THE REFERENC
C         -E TEMPERATURE
C***********************************************************************
          SUBROUTINE STENTH(SG1,T,TB,RNTH,TRW,HW,AMOL,P,N)
          DIMENSION SG1(25),TB(25),RNTH(25),TRW(25),HW(25),ENT(25),
          1AMOL(25),P(25,25)
          DO 10 I=2,N
          TBK=TB(I)+273.
          ENT(I)=((.3897*T+.0004638*(T**2))/(SG1(I)**(2./3.)))*
          1(.32651+.4515*(TBK/273.2+1.)**(1./3.)/SG1(I))
   10     CONTINUE
          ENT(1)=(2.266+7.913*(10.**-2)*TBK-2.647*(10.**-5)*(TBK**2)
          1-.674*(10.**-9)*(TBK**3))*T
          DO 20 I=1,N
          ENT(I)=ENT(I)/AMOL(I)
```

```
20    CONTINUE
      CPH=3.44
      HEN=CPH*T
      DO 30 I=6,N
      RNTH(I)=-(TRW(I)*ENT(I)+HEN*HW(I))
      DO 40 J=1,I-2
      RNTH(I)=RNTH(I)+ENT(J)*P(I,J)
40    CONTINUE
      RNTH(I)=RNTH(I)/TRW(I)
30    CONTINUE
      RETURN
      END
```

APPENDIX - B

PROGRAM DESCRIPTION FOR VACUUM DISTILLATE
HYDROTREATER MODEL

1) USAGE :

The program computes the temperature, sulfur concentration, mass fraction feed hydrocracked and the stoichiometric hydrogen consumption at the exit of the reactor. The main program initialises several variables, calls the subroutines DGIL, PROP and MOLFR. There are altogether 6 subroutines and 2 function subprograms all of which are written in FORTRAN.

2) SUBROUTINES REQUIRED:

SUBROUTINE DGIL: This subroutine uses the subroutine ENTHL as well as the subprograms RATCON and RATCR to solve the material and energy balance equations by Runge-Kutta-Gill method.

SUBROUTINE PROP:(same as in Appendix A)

SUBROUTINE ENTHL: (same as in Appendix A)

SUBROUTINE PHILN: (same as in Appendix A)

SUBROUTINE CUBEQ: (same as in Appendix A)

SUBROUTINE MOLFR: This subroutine converts mass fractions to mole fractions.

FUNCTION RATCON: This function subprogram calculates the second order rate constant for the hydrodesulfurisation reaction as a

function of temperature.

FUNCTION RATCR: This function subprogram calculates the first order rate constant for the hydrocracking reaction as a function of temperature.

3) DESCRIPTION OF THE PARAMETERS:

MAIN

PURMK	volume fraction hydrogen in make-up gas
PURRY	volume fraction hydrogen in the recycle gas
CF	characterisation factor
FT	total volumetric flow rate of the feed, m^3/h
FMA	mass flow rate of the pseudo-components, kg/h
FMF	mole fraction of the pseudo-components
AVMOL	average molecular weight of the liquid feed
HRCR	heat released during hydrocracking reaction, kcal/kg reactant
SHTRX	heat released during HDS reaction, kcal/kg sulfur reacting
TEM	temperature at the inlet of the reactor, K
CS	mass fraction sulfur in feed
CR	mass fraction of uncracked feed
CRØ	mass fraction of the uncracked feed at the reactor inlet
CSØ	mass fraction of sulfur in feed at the reactor inlet
SPCH	heat capacity of methane, kcal/kg
REC	volumetric flow rate of recycle gas, Nm^3/h
AMKUP	volumetric flow of the make-up gas, Nm^3/h
AMCH	molecular weight of methane
AMH	molecular weight of hydrogen
VH	total volumetric flow rate of the gas at the inlet of the reactor, Nm^3/h

H2	volumetric flow rate of hydrogen at the inlet, Nm^3/h
CH4	volumetric flow rate of methane at the inlet, Nm^3/h
AMOLH	average molecular weight of the gas at the inlet
RHOH	density of the gas mixture, kg/m^3
TOTALS	total sulfur in feed, kg/h
WCAT	weight of the catalyst bed, kg
QUENCH	volumetric flow rate of the quench stream, Nm^3/h
CPH	heat capacity of the gas stream, kcal/kg K
AMQ	molecular weight of the quench stream
CPQ	heat capacity of the quench stream, kcal/kg K
RHOQ	density of the quench stream, kg/Nm^3
QW	mass flow rate of the quench stream, kg/h
TOTCAT	total weight of the catalyst, kg
PT	average reactor pressure, atm
WH	mass flow rate of the gas stream, kg/h
HCON	hydrogen consumption rate, kg/h

SUBROUTINE DGIL:

CCØ	mass fraction of the pseudo-components
CSØ	mass fraction of sulfur compound in the reaction mixture
WCATØ	weight of catalyst, kg
FMF1	mole fraction of the pseudo-components
L1	=1 for liquid enthalpy
	=2 for vapour enthalpy
CPL	heat capacity of the liquid feed, kcal/kg K
SUL	heat generated during HDS reaction, kcal/(kg feed)(kg cat.)
CRK	heat generated during hydrocracking reaction, kcal/(kg feed)(kg cat.)

D1	change in the concentration of sulfur compound
D1R	fraction hydrocracked
DCM	$=dC_s/dW$
DCMR	$=dC_c/dW$
FMCPØ	$=\sum m_i C p_i$
DCE	$=dT/dW$

SUBROUTINE PROP: (same as in Appendix A)

SUBROUTINE ENTHL: (same as in Appendix A)

SUBROUTINE PHILN: (same as in Appendix A)

SUBROUTINE CUBEQ: (same as in Appendix A)

SUBROUTINE MOLFR:

CC	mass fraction of the components
AMOL	molecular weight of the pseudo-omponents
FMF	mol fraction of the pseudo-components
N	total number of pseudo-components

FUNCTION RATCON:

T	reaction temperature, K
RATCON	specific rate constant for the HDS reaction, (kg feed)^2/(kg cat.)(kg S)(h)

FUNCTION RATCR:

T	reaction temperature, K
RATCR	specific rate constant for the hydrocracking reaction, kg feed/(kg cat.)(h)

4) DIMENSION REQUIREMENTS:

The DIMENSION of the different parameters in the MAIN program as well as the subroutines has to be modified according to the requirements of a specific problem and is given in terms of the number of pseudo-components in the feed.

MAIN

DIMENSION CC(N),API(N),V(N),TB(N),SG(N),FM(N),OMEGA(N),PC(N),

TC(N),AMOL(N),VC(N),FMA(N),FMF(N),CF(N)

DGIL

DIMENSION CCØ(N),TBØ(N),SGØ(N),TCØ(N),VCØ(N),AMOLØ(N),OMEGA(N),

AM(N),FMF1(N),PCØ(N)

PROP   (same as in Appendix A)

ENTHL   (same as in Appendix A)

PHILN   (same as in Appendix A)

CUBEQ   (same as in Appendix A)

MOLFR

DIMENSION CC(N),AMOL(N),FMF(N),AM(N)

5) INPUTS TO BE SUPPLIED:

1) Total number of pseudo-components

2) Volumetric flow rate of the feed, m^3/h

3) Density of the feed, kg/m^3

4) Volumetric composition of the pseudo-components, vol.%

5) Mid-boiling point of the pseudo-components, $^{\circ}$C

6) Specific gravity of the pseudo-components

7) Mass fraction sulfur in feed

8) Purity of the recycle and make-up gas, volume fraction

9) Volumetric flow rate of the recycle and make-up gas, Nm^3/h

10) Heat of reaction for the HDS reaction, kcal/kg S reacting;

and for the hydrocracking reaction, kcal/kg feed cracked.

11) Total number of beds and number of integration steps.

12) Reactor inlet temperature, K; and average pressure, atm.

```
C********************************************************************
C          PROGRAM FOR MODELING OF VACUUM DISTILLATE HYDROTREATER
C
C********************************************************************
          DIMENSION CC(25),API(25),V(25),TB(25),SG(25),FM(25),OMEGA(25)
     1    ,PC(25),TC(25),AMOL(25),VC(25),FMA(25),FMF(25),CF(25)
          OPEN(UNIT=22,DEVICE='DSK',FILE='VAC.IN')
          READ(22,*) (TB(I),I=1,14)
          READ(22,*) (SG(I),I=1,14)
          READ(22,*) (V(I),I=1,14)
          N=14
C********************************************************************
C          N=TOTAL NO. OF PSEUDO-COMPONENTS
C          PURMK=PURITY OF THE MAKE-UP GAS
C          PURRY=PURITY OF THE RECYCLE GAS
C********************************************************************
          PURMK=.953;PURRY=.787
          CALL PROP(TB,SG,N,TC,PC,VC,AMOL,OMEGA)
          DO  13 I=1,N
          CF(I)=((TB(I)*9./5.)+492.)**(1./3.)/SG(I)
   13     CONTINUE
C         WRITE(63,*) TB,SG,CF,TC,PC,VC,OMEGA,AMOL
          RHOB=721.
          RHOF=920.
          SUM=0.
          FT=43.7
          SUMF=RHOF*FT
          DO 40 I=1,N
          FM(I)=V(I)*SG(I)*1000.
          SUM=SUM+FM(I)
   40     CONTINUE
          DO 50 I=1,N
          CC(I)=FM(I)/SUM
          FMA(I)=SUMF*CC(I)
   50     CONTINUE
          CALL MOLFR(CC,AMOL,FMF,N)
          AVMOL=0.
          DO 10 I=1,N
          AVMOL=AVMOL+FMF(I)*AMOL(I)
   10     CONTINUE
          HRCR=10000./AVMOL
          SHTRX=1855.
          TEM=631.
          CS=.034
          CR=1.
          CR0=CR
          CS0=CS
C********************************************************************
C          AMKUP= VOL. FLOW RATE OF THE MAKE-UP GAS
C          AMCH=MOL. WT. OF METHANE
C          AMH=MOL. WT. OF HYDROGEN
C          SPCH=SP. HEAT OF METHANE AT REACTION CONDITIONS
C          SPH=SP. HEAT OF HYDROGEN AT REACTION CONDITIONS
C********************************************************************
          REC=7240.;AMKUP=4000.;AMCH=16.;AMH=2.0
          SPCH=.8286;SPH=3.4865
          VH=REC+AMKUP
```

```
      H2=REC*PURRY+AMKUP*PURMK
      CH4=VH-H2
      AMOLH=(CH4*AMCH+H2*AMH)/VH
      RHOH=AMOLH*1000./(82.06*273.)
      TOTALS=SUMF*CS
C************************************************************************
C         N1=NO. OF BEDS
C         N2=NO OF STEPS
C         WCAT=WEIGHT OF CATALYST BED
C************************************************************************
      N1=3
      N2=25
      VCAT=6.4
      QUENCH=6630.
      CPH=(CH4*SPCH*AMCH+H2*SPH*AMH)/(VH*AMOLH)
      AMQ=PURRY*AMH+(1.-PURRY)*AMCH
      CPQ=((1.-PURRY)*SPCH*AMCH+PURRY*SPH*AMH)/AMQ
      RHOQ=AMQ*1000./(82.06*273.)
      QW=QUENCH*RHOQ
      FHCP=QW*CPQ
      TOTCAT=0.
      PT=950./14.7
      DO 69 I=1,N1
      WCAT=VCAT*RHOB
      TOTCAT=TOTCAT+WCAT
      WH=VH*RHOH
      CALL DGIL(CC,CS0,N,WCAT,N2,TEM,FMCP,RHOB,TB,SUMF,T2,SHTRX,
     1 SG,WH,CPH,TC,VC,AMOL,OMEGA,PC,PT,HRCR,CR0)
      VH=VH+QUENCH
      IF(I.EQ.1)VCAT=10.3
      IF(I.EQ.2)VCAT=18.2
      IF(I.EQ.3)GO TO 30
      TH2=338.6
      TEM=(FMCP*T2+FHCP*TH2)/(FMCP+FHCP)
      CPH=(CPQ*QW+WH*CPH)/(QW+WH)
      AMOLH=(QUENCH*AMQ+VH*AMOLH)/(QUENCH+VH)
      RHOH=AMOLH*1000./(82.06*273.)
30    WRITE(63,45) T2,TEM,CS0,I
45    FORMAT(4X,'OUTLET TEMP=',F6.2,'K',2X,'INLET TEMP TO NEXT BED=',
     1 F6.2,'K',2X,'OUTLET SULFUR CONC=',F6.4,2X,'BED NUMBER=',I2//)
      IF(I.EQ.3) GO TO 35
69    CONTINUE
35    HCON=((CS-CS0)*8./32.+(CR-CR0)*2./AVMOL)*SUMF
      WRITE(63,46) HCON
46    FORMAT(4X,'H2 CONSUMED=',F8.2,'KG'//)
      STOP
      END


C************************************************************************
C         THIS SUBROUTINE USES THE RUNGE - KUTTA - GILL METHOD TO
C         INTEGRATE THE DIFFERENTIAL HEAT AND MASS BALANCE EQUATIONS
C         NUMERICALLY.
C************************************************************************
      SUBROUTINE DGIL(CC0,CS0,N0,WCAT0,N20,TEM0,FMCP0,RHOB,TB0,
     1 SUMF0,T20,SHTRX,SG0,WH0,CPH0,TC0,VC0,AMOL0,OMEGA,PC0,PT0
     1 ,HRCR0,CR0)
```

```
      DIMENSION CCØ(25),TBØ(25),SGØ(25),TCØ(25),VCØ(25),AMOLØ(25)
1    ,OMEGA(25),A(4),B(4),C(4),AM(25),FMF1(25),PCØ(25)
      X=Ø.
      X1=1.
      N1=1
      H=(X1-X)/(FLOAT(N2Ø))
      D6=H*.5
      X=X+D6
      QQ=Ø.
      Q=Ø.
      QR=Ø.
      A(1)=.5
      B(1)=2.
      C(1)=.5
      A(2)=1.-SQRT(.5)
      B(2)=1.
      C(2)=A(2)
      A(3)=1.+SQRT(.5)
      B(3)=1.
      C(3)=A(3)
      A(4)=1./6.
      B(4)=2.
      C(4)=.5
      CALL MOLFR(CCØ,AMOLØ,FMF1,NØ)
      L1=1
      CALL ENTHL(TCØ,PCØ,OMEGA,PTØ,TEMØ,FMF1,ENTH1,SGØ,TBØ,NØ,AMOLØ
     1,L1,CCØ)
      CPL=ENTH1/(TEMØ-273.)
4     DO 3 J=1,4
      DC=-RATCON(TEMØ)*(CSØ**2)
      DCR=-RATCR(TEMØ)*CRØ
      DCM=DC*WCATØ/SUMFØ
      DCMR=DCR*WCATØ/SUMFØ
      SUL=SHTRX*RATCON(TEMØ)*(CSØ**2)
      CRK=HRCRØ*RATCR(TEMØ)*CRØ
      DCOH=SUL+CRK
      D=A(J)*(DCM-B(J)*Q)
      DR=A(J)*(DCMR-B(J)*QR)
      D1=H*D
      D1R=H*DR
      CSØ=CSØ+D1
      CRØ=CRØ+D1R
      D2=D*3.
      D2R=DR*3.
      D3=C(J)*DCM
      D3R=C(J)*DCMR
      D2=D2-D3
      D2R=D2R-D3R
      Q=Q+D2
      QR=QR+D2R
      FMCPØ=(WHØ*CPHØ)+SUMFØ*CPL
      DCE=DCOH*WCATØ/FMCPØ
      DD=A(J)*(DCE-B(J)*QQ)
      DD1=H*DD
      TEMØ=TEMØ+DD1
      DD2=DD*3.
      DD3=C(J)*DCE
```

```
      DD2=DD2-DD3
      QQ=QQ+DD2
      IF(J.GT.1) GO TO 2
      GO TO 3
    2 IF(J.GT.2) GO TO 3
      X=X+D6
    3 CONTINUE
      WRITE(63,48) N1,X,TEMØ,CSØ,CRØ
   48 FORMAT (2X,'STEP NO.=',I3,2X,'FRACT. WEIGHT OF THE BED=',F4.2,
    1 2X,'TEMPERATURE=',F7.2,'K',2X,'SULFUR CONC.=',F6.4,2X,'UNCRACKED

    1  CONC.=',F6.4//)
      IF(N1.EQ.N2Ø)GO TO 5
      N1=N1+1
      IF(X.GT.X1) GO TO 5
      X=X+D6
      GO TO 4
    5 T2Ø=TEMØ
      RETURN
      END
```

```
C***********************************************************************
        SUBROUTINE PROP (same as in Appendix A)
C***********************************************************************

C***********************************************************************
        SUBROUTINE ENTHL (same as in Appendix A)
C***********************************************************************

C***********************************************************************
        SUBROUTINE PHILN (same as in Appendix A)
C***********************************************************************

C***********************************************************************
        SUBROUTINE CUBEQ (same as in Appendix A)
C***********************************************************************

C***********************************************************************
C       THIS SUBROUTINE CONVERTS MASS FRACTIONS TO MOLE FRACTION
C***********************************************************************
        SUBROUTINE MOLFR(CC,AMOL,FMF,N)
        DIMENSION CC(25),AMOL(25),FMF(25),AM(25)
        SUM=Ø.
        DO 1Ø I=1,N
        AM(I)=CC(I)/AMOL(I)
        SUM=SUM+AM(I)
   1Ø   CONTINUE
        DO 2Ø I=1,N
        FMF(I)=AM(I)/SUM
   2Ø   CONTINUE
        RETURN
        END
```

```
C***********************************************************************
C       THIS FUNCTION CALCULATES THE RATE CONSTANT FOR THE DESULFURI-
C       SATION REACTION
C***********************************************************************
        FUNCTION RATCON(T)
```

```fortran
      RATCON=2.92E+11*EXP(-13500./T)
      RETURN
      END

C*********************************************************************
C        THIS FUNCTION SUBPROGRAM CALCULATES THE RATE CONSTANT FOR THE
C        CRACKING REACTION
C*********************************************************************
      FUNCTION RATCR(T)
      RATCR=4.11E+07*EXP(-13416./T)
      RETURN
      END
```

APPENDIX - C

PROGRAM DESCRIPTION FOR KEROSENE HYDROTREATER MODEL

1) USAGE

The program computes the temperature and sulfur concentration along the length of the reactor as well as the stoichiometric hydrogen consumption and molar flow rate at the exit of the reactor. The main program initialises certain variables and calls the major subroutine DGIL. There are altogether 8 subroutines and 3 function subprograms all of which are written in FORTRAN.

2) SUBROUTINES REQUIRED

SUBROUTINE DGIL : This subroutine uses the Runge-Kutta-Gill method to integrate the differential material and energy balance equations. It uses the subroutines ENTHL, MIXHY, MFRAC and also the subprograms RATCON.

SUBROUTINE PROP: (Same as in Appendix A)

SUBROUTINE ENTHL: This subroutine calculates the enthalpy of the reaction mixture.

SUBROUTINE PHILN: This subroutine calculates the partial fugacity coefficient of the components.

SUBROUTINE CUBEQ: (Same as in Appendix A)

SUBROUTINE MFRAC: This subroutine calculates the mole fraction of the components from the molar flow rate.

SUBROUTINE MIXHY: This subroutine calculates the critical

properties of the hydrogen gas mixture.

SUBROUTINE INTRCT: This subroutine calculates the binary interaction parameter required in the calculation of critical properties of the hydrogen gas mixture.

FUNCTION RATCON: Estimates the rate constant for the desulfurisation reaction.

FUNCTION CP: Estimates the ideal gas enthalpy for hydrogen and methane.

3) DESCRIPTION OF THE PARAMETERS

MAIN:

NC	number of components in the gas mixture
TCX,PCX, VCX,	critical temperature, critical pressure, critical volume; K, atm, cm^3/gmol respectively.
OMX	acentric factor of the components in the hydrogen gas mixture
AMOX	molecular weight of the components in the hydrogen gas mixture
FMO	molar flow rate of the pseudo-components, kmol/h
AMX	molar flow rate of the different components in the hydrogen gas mixture, kmol/h
CPM	ideal gas heat capacity of the hydrogen gas mixture, kcal/kmol
AMF	molar concentration of the hydrogen gas mixture
GAMA	interaction parameter
TC1,PC1, VC1	critical temperature, pressure, volume of the hydrogen gas mixture; K, atm, cm^3/gmol
OM1,AML	acentric factor and molecular weight of the hydrogen gas mixture

AVMOL   average molecular weight of the feed

PTOT   molar flow rate of the oil feed, kmol/h

HTOT   molar flow rate of the hydrogen gas mixture, kmol/h

TOTMOL   total molar flow rate, kmol/h

YO   molar concentration of the components in the reaction mixture

SHTRX   heat released during HDS reaction, kcal/kmol

CS   mass fraction sulfur in feed

CSØ   mass fraction sulfur in product

YS   mole fraction sulfur in the reaction mixture at the reactor inlet

YSØ   mole fraction sulfur in the reaction mixture at any time

TOTALS   sulfur flow rate, kg/h

SUBROUTINE DGIL:

YOØ   mole fraction of the components including hydrogen gas mixture

YSØ   mole fraction of sulfur in the liquid phase

SHTRX   heat released during HDS reaction, kcal/kmol S

WHØ   mass flow rate of the hydrogen gas mixture, kg/h

TCØ,VCØ   critical temperature, K; critical volume, cm^3/gmol;
PCØ   critical pressure, atm

AMOLØ   molecular weight and acentric factor of the components
OMEGA

PTØ   average reactor pressure, atm

CPM   heat capacity of the reaction mixture, kcal/kmol K

AMX   molar flow rate of the components in the hydrogen gas mixture, kmol/h

XTOT   molar flow rate of the hydrogen gas mixture at each increment, kmol/h

FMO   mass flow rates of the different components, kg/h

ZØ   compressibility factor of the reaction mixture

SUBROUTINE PROP: (same as in Appendix A)

SUBROUTINE ENTHL:

Y   molar concentration of the components

ENTH   enthalpy of the mixture, kcal/kmol

CPMØ   average molar specific heat of the gas mixture, kcal/kmol K

SUBROUTINE PHILN: (parameter description is the same as in Appendix A although the argument list is different)

SUBROUTINE CUBEQ: (same as in Appendix A)

SUBROUTINE MIXHY:

AMF   molar concentration of the gas mixture

AMOX   molecular weight of the components

TCX,PCX   critical properties of the components
VCX,OMX

TC1,PC1   mixture critical properties
OM1,VC1

AML   molecular weight of the gas mixture

GAMA   interaction parameter for calculating the mixture critical volume

N   total number of components

THE,THET   factors in the correlations for calculating the mixture critical volume and temperature respectively

Z   mixture critical compressibilty factor

SUBROUTINE INTRCT:

TCX,PCX   critical properties of the components
VCX,OMX

AT,AV   constants in the correlation for calculating the mixture critical volume

SIV   factor in the calculation of the interaction parameter

SUBROUTINE MFRAC:

AMX   moles of each components

AMF   mole fraction of the components

N   total number of components

FUNCTION RATCON :

T   reaction temperature, K

RATCON   specific rate constant for the HDS reaction

FUNCTION CP :

TEM   reaction temperature, K

I   =1 for hydrogen

             =2 for methane

             =3 for hydrogen sulfide

             =4 for ethane

             =5 for propane

CP   heat capacity of an ideal gas, kcal/kmol K

4) DIMENSION REQUIREMENTS:

The minimum DIMENSION of the parameters in the MAIN program as well as the subroutines is given in terms of N (total number of pseudo-components) and NC (the total number of components in the hydrogen gas mixture)

MAIN:

DIMENSION   CC(N),API(N),V(N),TB(N),SG(N),FM(N),OMEGA(N+1),PC(N+1),
            TC(N+1),AMOL(N+1),VC(N+1),FMA(N),YO(N+1),AMX(NC),CF(N),
            TCX(NC),PCX(NC),VCX(NC),OMX(NC),GAMA(NC,NC),FMO(N+1)
            AMF(NC),AMOX(NC)

SUBROUTINE DGIL:

DIMENSION   TBØ(N),AMOLØ(N+1),OMEGA(N+1),TCØ(N+1),VCØ(N+1),A(4),
            B(4),C(4),PCØ(N+1),ZØ(N+1,3),AMX(NC),YOØ(N+1),AMOX(NC),
            TCX(NC),VCX(NC),OMX(NC),PCX(NC),AMF(NC),FMO(N+1)

SUBROUTINE ENTHL:

DIMENSION TC(N+1),PC(N+1),OMEGA(N+1),Y(N+1),SG1(N),TBPP(N)

           HILN(N+2),PHIL1(N+2),PHI(N+2),PHI(N+2),AMW(N+1)

           HID(N+1),TBPR(N)

SUBROUTINE PHILN:

DIMENSION TC(N+1),PC(N+1),OMEGA(N+1),Y(N+1),A(N+2),B(N+2)

           Z(N+2,3),ALFAA(N+1),HILN(N+2),PHI(N+2),TR(N+1)

           YALF(N+1),A1(N+1),B1(N+1)

SUBROUTINE CUBEQ:

DIMENSION AØ(N+2),BØ(N+2),ZØ(N+2,3)

SUBROUTINE MFRAC:

DIMENSION AMX(NC),AMF(NC)

SUBROUTINE MIXHY

DIMENSION AMF(NC),AMOX(NC),TCX(NC),PCX(NC),OMX(NC),VCX(NC)

           GAMA(NC,NC),THE(NC),THET(NC)

SUBROUTINE INTRCT:

DIMENSION TCX(NC),PCX(NC),VCX(NC),OMX(NC),GAMA(NC,NC),AT(NC)

           AV(NC)

5) INPUTS TO BE SUPPLIED

 1) Total number of pseudo-components

 2) Total number of components in the hydrogen gas mixture

 3) Either the purity of the hydrogen gas mixture

 4) Mid-boiling points of the pseudo-components, $^{\circ}C$

 5) Specific gravity of the pseudo-components

 6) Total volumetric feed rate, m^3/h

 7) Volumetric composition of the feed

8) Density of the catalyst bed, kg/m^3

9) Critical properties and the molecular weights of the components in the gas mixture

10) Reactor inlet temperature (K) and pressure (atm)

11) Mass fraction sulfur in feed

12) Volumetric flow rate of the recycle and make-up gas, Nm^3/h

13) Volume of catalyst per bed, m^3

```
C******************************************************************
C         PROGRAM FOR MODELING OF  KEROSENE HYDROTREATER
C
C******************************************************************
          DIMENSION CC(25),API(25),V(25),TB(25),SG(25),FM(25),OMEGA(25)
     1    ,PC(25),TC(25),AMOL(25),VC(25),FMA(25),FMO(25),YO(25),AMX(5)
     1    ,CF(25),TCX(5),PCX(5),VCX(5),OMX(5),GAMA(5,5),AMF(5),AMOX(5)
          COMMON TOTMOL,PTOT,HTOT,AMX,NC,AMF,FMO,GAMA
          COMMON/AREA1/TCX,PCX,VCX,OMX,AMOX
          OPEN(UNIT=54,DEVICE='DSK',FILE='KERO.OUT')
          OPEN(UNIT=53,DEVICE='DSK',FILE='KERO.RES')
          READ(54,*) (TB(I),I=1,10)
          READ(54,*) (API(I),I=1,10)
          READ(54,*) (V(I),I=1,10)
          PTOT=0.
          N=10
          NC=2
          DO 23 I=1,N
          SG(I)=141.5/(API(I)+131.5)
   23     CONTINUE
          CALL PROP(TB,SG,N,TC,PC,VC,AMOL,OMEGA)
          TCX(1)=41.2;PCX(1)=20.8;VCX(1)=65.;OMX(1)=0.;AMOX(1)=2.017
          TCX(2)=190.6;PCX(2)=45.4;VCX(2)=99.;OMX(2)=.008;AMOX(2)=16.
          DO 13 I=1,N
          CF(I)=((TB(I)*9./5.)+492.)**(1./3.)/SG(I)
   13     CONTINUE
C         WRITE(53,*)SG,TB,TC,PC,VC,AMOL,OMEGA,CF
C         BULK DENSITY=45 LBS/FT**3
          PURRY=.70;PURMK=.82
C         PURRY=.86;PURMK=.89
C         PURRY=.68;PURMK=.72
          RHOB=721.
          RHOF=808.
          SUM=0.
          FT=75.
C         FT=83.
C         FT=73.
          SUMF=RHOF*FT
          DO 40 I=1,N
          FM(I)=V(I)*SG(I)*1000.
          SUM=SUM+FM(I)
   40     CONTINUE
          DO 50 I=1,N
          CC(I)=FM(I)/SUM
          FMA(I)=SUMF*CC(I)
          FMO(I)=FMA(I)/AMOL(I)
          PTOT=PTOT+FMO(I)
   50     CONTINUE
          SHTRX=59361.
C         TEM=581.
          TEM=568.
C         TEM=570.
          CPM=0.
          DO 8 I=1,2
          K=I
          CPM=CPM+CP(TEM,K)
   8      CONTINUE
```

```
C           CS=.0055
C           CS=.0049
            CS=.0033+.002
            REC=250.;AMKUP=1300.
C           REC=250.;AMKUP=1410.
C           REC=0.;AMKUP=1650.
            VH=REC+AMKUP
            H2=PURRY*REC+PURMK*AMKUP
            CH4=VH-H2
            AMF(1)=H2/VH;AMF(2)=CH4/VH
            CALL INTRCT(GAMA,NC)
            CALL MIXHY(AMF,AMOX,TCX,PCX,OMX,VCX,TCM,PCM,OMGM,VCM
     1      ,AMOH,GAMA,NC)
            TC(N+1)=TCM;PC(N+1)=PCM;VC(N+1)=VCM;OMEGA(N+1)=OMGM
            AMOL(N+1)=AMOH
            RHOH=AMOL(N+1)*1000./(82.06*273.)
            TOTALS=SUMF*CS
            HTOT=VH*RHOH/AMOH
            DO 15 I=1,NC
            AMX(I)=AMF(I)*HTOT
   15       CONTINUE
            TOTMOL=PTOT+HTOT
            WRITE (53,34) TOTMOL
   34       FORMAT (4X,'NO. OF MOLES AT THE REACTOR INLET=',F8.2//)
            YS=TOTALS/(TOTMOL*32.)
            YS0=YS
            DO 76 I=1,N
            YO(I)=FMO(I)/TOTMOL
   76       CONTINUE
            YO(N+1)=VH*RHOH/(AMOH*TOTMOL)
C******************************************************************
C           N1=NO. OF BEDS
C           N2=NO OF STEPS
C           WCAT=WEIGHT OF CATALYST BED
C******************************************************************
            N1=1
            N2=25
            VCAT=15.5
            WCAT=VCAT*RHOB
            TOTCAT=0.
            PT=24.
            DO 69 I=1,N1
            TOTCAT=TOTCAT+WCAT
            WH=VH*RHOH
            CALL DGIL(YO,YS0,N,WCAT,N2,TEM,RHOB,TB,SUMF,T2,SHTRX,
     1      SG,TC,VC,AMOL,OMEGA,PC,PT,CPM)
            CS0=YS0*32.*TOTMOL/SUMF
            WRITE(53,36) TOTMOL
   36       FORMAT (4X, 'NO. OF MOLES AT THE REACTOR OUTLET=', F8.2//)
   30       WRITE(53,45) T2,TEMP,CS0,I
   45       FORMAT(4X,'OUTLET TEMP=',F6.2,'K',2X,'INLET TEMP TO NEXT BED=',
     1      F6.2,'K',2X,'OUTLET SULFUR CONC=',F6.4,2X,'BED NUMBER=',I2//)
            IF(I.EQ.3) GO TO 35
   69       CONTINUE
   35       HCON=(CS-CS0)*SUMF*8./32.
            WRITE(53,46) HCON
   46       FORMAT(4X,'H2 CONSUMED=',F8.2,'KG'//)
```

```
            STOP
            END



C**************************************************************
C       THIS SUBROUTINE INTEGRATES THE DIFFERENTIAL MASS BALANCE AND
C       ENERGY BALANCE EQUATIONS USING THE RUNGE - KUTTA - GILL
C       METHOD.
C**************************************************************
            SUBROUTINE DGIL(YOØ,YSØ,NØ,WCATØ,N2Ø,TEMØ,RHOB,TBØ,
      1     SUMFØ,T2Ø,SHTRX,SGØ,TCØ,VCØ,AMOLØ,OMEGA,PCØ,PTØ,CPM)
            COMMON TOTMOL,PTOT,HTOT,AMX,NC,AMF,FMO,GAMA
            COMMON/AREA1/TCX,PCX,VCX,OMX,AMOX
            DIMENSION CCØ(25),TBØ(25),SGØ(25),TCØ(25),VCØ(25),AMOLØ(25)
      1     ,OMEGA(25),A(4),B(4),C(4),PCØ(25),ZØ(26,3),AMX(5)
      1     ,YOØ(25),AMOX(5),TCX(5),VCX(5),OMX(5),PCX(5),AMF(5),FMO(25)
      1     ,GAMA(5,5)
            X=Ø.
            X1=1.
            N1=1
            H=(X1-X)/(FLOAT(N2Ø))
            D6=H*.5
            X=X+D6
            QQ=Ø.
            Q=Ø.
            A(1)=.5
            B(1)=2.
            C(1)=.5
            A(2)=1.-SQRT(.5)
            B(2)=1.
            C(2)=A(2)
            A(3)=1.+SQRT(.5)
            B(3)=1.
            C(3)=A(3)
            A(4)=1./6.
            B(4)=2.
            C(4)=.5
            SGM=Ø.
            DO 20 I=1,NØ
            SGM=SGM+YOØ(I)*SGØ(I)
      20    CONTINUE
      4     DO 3 J=1,4
            CPM=Ø.
            DO 8 I=1,2
            K=I
            CPM=CPM+CP(TEMØ,K)
      8     CONTINUE
            L1=2
            CALL ENTHL(TCØ,PCØ,OMEGA,PTØ,TEMØ,YOØ,ENTH1,SGØ,TBØ,NØ+1,AMOLØ
      1     ,L1,CPM,ZØ)
            CPV=ENTH1/(TEMØ-273.)
            R=.Ø82Ø6
            DC=-RATCON(TEMØ)*PTØ**2*(YSØ**2)/((ZØ(12,1)*R*TEMØ)**2)
            DCM=DC*WCATØ/(TOTMOL)
            DCOH=SHTRX*RATCON(TEMØ)*(YSØ**2)*(PTØ/(ZØ(12,1)*R*TEMØ))**2
            D=A(J)*(DCM-B(J)*Q)
```

```
         D1=H*D
         TOT1=TOTMOL
         AMX(1)=AMX(1)+D1*TOTMOL*4.
         CALL MFRAC(AMX,AMF,NC)
         CALL MIXHY(AMF,AMOX,TCX,PCX,OMX,VCX,TC1,PC1,OM1,VC1,AML,
       1 GAMA,NC)
         XTOT=0.
         DO 19 I=1,NC
         XTOT=XTOT+AMX(I)*AMOX(I)
      19 CONTINUE
         HTOT=XTOT/AMOLØ(NØ+1)
         FMO(NØ+1)=HTOT
         CALL MFRAC(FMO,YOØ,NØ+1)
         AMOLØ(NØ+1)=AML; PCØ(NØ+1)=PC1;VCØ(NØ+1)=VC1; TCØ(NØ+1)=TC1
         OMEGA(NØ+1)=OM1
         YSØ=YSØ+D1
         D2=D*3.
         D3=C(J)*DCM
         D2=D2-D3
         Q=Q+D2
         FMCPØ=TOTMOL*CPV
         DCE=DCOH*WCATØ/FMCPØ
         DD=A(J)*(DCE-B(J)*QQ)
         DD1=H*DD
         TEMØ=TEMØ+DD1
         DD2=DD*3.
         DD3=C(J)*DCE
         DD2=DD2-DD3
         QQ=QQ+DD2
         TOTMOL=PTOT+HTOT
         YSØ=YSØ*TOT1/TOTMOL
         IF(J.GT.1) GO TO 2
         GO TO 3
       2 IF(J.GT.2) GO TO 3
         X=X+D6
       3 CONTINUE
         CSØ=YSØ*32.*TOTMOL/SUMFØ
         WRITE(53,48) N1,X,TEMØ,CSØ
      48 FORMAT (2X,'STEP NO.=',I3,2X,'FRACT. WEIGHT OF THE BED=',F4.2,
       1 2X,'TEMPERATURE=',F7.2,'K',2X,'SULFUR CONC.=',F6.5//)
         IF(N1.EQ.N2)GO TO 5
         N1=N1+1
         IF(X.GT.X1) GO TO 5
         X=X+D6
         GO TO 4
       5 T2Ø=TEMØ
         RETURN
         END


C*********************************************************************
         SUBROUTINE PROP (same as that in Appendix A)
C*********************************************************************
```

```
C*********************************************************************
C         THIS SUBROUTINE ESTIMATES THE ENTHALPIES ON THE BASIS OF
C         PENG-ROBINSON'S EQUATION OF STATE
C*********************************************************************
          SUBROUTINE ENTHL(TC,PC,OMEGA,PT,T,Y,ENTH,SG1,TBPP,N,AMW,L1,CPM
          1,Z)
          DIMENSION TC(25),PC(25),OMEGA(25),Y(25),SG1(25),TBPP(25),
          1HILN(26),PHIL1(26),PHI(26),PHI1(26),AMW(25),HID(25)
          1,Z(26,3)
          CALL PHILN(TC,PC,OMEGA,PT,T,Y,HILN,PHI,N,2,L1,Z)
          CALL PHILN(TC,PC,OMEGA,PT,(T*1.0001),Y,PHIL1,PHI1,N,2,L1,Z)
          HEX=0.
          DO 10 I=1,N
          HEX=HEX+((PHIL1(I)-HILN(I))*Y(I)/(.0001*T))
   10     CONTINUE
          R=1.987
          HEX=-R*(T**2)*HEX
          TR=(T-273.)*9./5.+492.
          TF=(T-273.)*9./5.+32.
          HIDL=0.
          DO 20 I=1,N-1
          HID(I)=215.-87.*SG1(I)+(.415-.104*SG1(I))*TF+(.000310-.000078*SG
          11(I))*TF**2
          HIDL=HIDL+Y(I)*HID(I)*AMW(I)*252./453.5
   20     CONTINUE
          HID(N)=CPM*(T-273.)
          A=Y(N)*HID(N)
          HIDL=HIDL+Y(N)*HID(N)
          ENTH=HEX+HIDL
          RETURN
          END


C*********************************************************************
C         THIS SUBROUTINE ESTIMATES THE FUGACITY CO-EFFICIENTS BASED ON
C         PENG ROBINSON'S EQUATION OF STATE
C*********************************************************************
          SUBROUTINE PHILN(TC,PC,OMEGA,PT,T,Y,HILN,PHI,N,L,L1,Z)
          DIMENSION TC(25),PC(25),OMEGA(25),Y(25),A(26),B(26),Z(26,3)
          1,ALFAA(25),HILN(26),PHI(26),TR(25),YALF(25),A1(25),B1(25)
          DO 10 J=1,N
          TR(J)=T/TC(J)
          YALF(J)=0.
          R=.08205
          A1(J)=.45724*(R**2)*(TC(J)**2)/(PC(J))
          B1(J)=.07780*R*TC(J)/PC(J)
          ALFA=(1.+(.37464+(1.54226*OMEGA(J))-(.26992*(OMEGA(J)**2)))*(1.-
          1(TR(J)**.5)))**2
          ALFAA(J)=ALFA*A1(J)
          A(J)=ALFAA(J)*PT/((R**2)*(T**2))
          B(J)=B1(J)*PT/(R*T)
   10     CONTINUE
          IF(L.EQ.1)GO TO 70
          A(N+1)=0.
          B(N+1)=0.
          ALF=0.
          DO 20 J=1,N
          B(N+1)=B(N+1)+B(J)*Y(J)
```

```
            DO 30 I=1,N
            A(N+1)=A(N+1)+Y(I)*Y(J)*((A(J)*A(I))**.5)
            ALF=ALF+(Y(I)*Y(J))*SQRT(ALFAA(I)*ALFAA(J))
            YALF(J)=YALF(J)+Y(I)*SQRT(ALFAA(I)*ALFAA(J))
    30      CONTINUE
    20      CONTINUE
    70      CALL CUBEQ(A,B,N,Z,L,L1)
            IF(L.EQ.1)GO TO 80
            DO 40 I=1,N
            HILN(I)=(B(I)/B(N+1))*(Z(N+1,1)-1.)-(ALOG(Z(N+1,1)-B(N+1)))+(A(N
           1+1)/(4.828*B(N+1)))*(B(I)/B(N+1)-(2.*YALF(I)/ALF))*(ALOG((Z(N+1
           1,1)+2.414*B(N+1))/(Z(N+1,1)-.414*B(N+1))))
    40      CONTINUE
            GO TO 100
    80      DO 90 I=1,N
            PHI(I)=Z(I,1)-1.-ALOG(Z(I,1)-B(I))-(A(I)/(B(I)*4.828))*ALO
           1G((Z(I,1)+(2.414*B(I)))/(Z(I,1)-(.414*B(I))))
    90      CONTINUE
   100      RETURN
            END


C********************************************************************
            SUBROUTINE CUBEQ (same as that in Appendix A)
C********************************************************************

C********************************************************************
C           THIS SUBROUTINE ESTIMATES THE MIXTURE CRITICAL PROPERTIES
C********************************************************************
            SUBROUTINE MIXHY (AMF,AMOX,TCX,PCX,OMX,VCX,TC1,PC1,OM1,VC1
           1 ,AML,GAMA,N)
            DIMENSION AMF(5),AMOX(5),TCX(5),PCX(5),OMX(5),VCX(5),
           1 GAMA(5,5),THE(5),THET(5)
            AML=0.;OM1=0.;PC1=0.;VC1=0.
            R=82.04
            TC1=0.;SUM1=0.
            SUM=0.
            DO 1 I=1,N
            OM1=OM1+OMX(I)*AMF(I)
            AML=AML+AMOX(I)*AMF(I)
            SUM=SUM+AMF(I)*VCX(I)**(2./3.)
            SUM1=SUM1+AMF(I)*VCX(I)
    1       CONTINUE
            DO 2 I=1,N
            THE(I)= AMF(I)*VCX(I)**(2./3.)/SUM
            THET(I)=AMF(I)*VCX(I)/SUM1
    2       CONTINUE
            DO 3 J=1,N
            TC1=TC1+THET(J)*TCX(J)
            VC1=VC1+THE(J)*VCX(J)
            DO 4 I=1,N
            VC1=VC1+THE(I)*THE(J)*GAMA(I,J)
    4       CONTINUE
    3       CONTINUE
            Z=.2905-.085*OM1
            PC1=Z*R*TC1/VC1
   10       RETURN
            END
```

```
C**********************************************************************
C        THIS SUBROUTINE CALULATES THE INTERACTION PARAMETERS REQUIRED
C        FOR ESTIMATING THE CRITICAL PROPERTIES
C**********************************************************************
        SUBROUTINE INTRCT (GAMA,N)
        DIMENSION TCX(5),PCX(5),VCX(5),OMX(5),ENTER(5,5),GAMA(5,5)
     1  ,AT(5),AV(5),OMA(5)
        COMMON /AREA1/TCX,PCX,VCX,OMX
        R=82.04
        AT(1)=-.4957;AT(2)=17.1185;AT(3)=-168.56;AT(4)=587.05
        AT(5)=-698.89
        AV(1)=.1397;AV(2)=-2.9672;AV(3)=1.8337;AV(4)=-1.536
        AV(5)=0.
        DO 1 I=1,N
        DO 1 J=1,N
        IF(I.EQ.J)GO TO 1
        DV=ABS((VCX(I)**(2./3.)-VCX(J)**(2./3.))/(VCX(I)**(2./3.)
     1  +VCX(J)**(2./3.)))
        SIV=0.
        DO 2 K=1,N
        IF (I.EQ.3.OR.J.EQ.3) GO TO 8
        SIV=SIV+AV(K)*DV**(K-1)
        GO TO 2
    8   SIV=SIV+AT((K))*DV**(K-1)
    2   CONTINUE
        GAMA(I,J)=SIV*(VCX(I)+VCX(J))/2.
    1   CONTINUE
        RETURN
        END


C**********************************************************************
C        THIS SUBROUTINE CALCULATES THE MOLE FRACTION GIVEN THE MOLAR
C        FLOW RATES
C**********************************************************************
        SUBROUTINE MFRAC(AMX,AMF,N)
        DIMENSION AMX(5),AMF(5)
        TOT=0.
        DO 1 I=1,N
        TOT=TOT+AMX(I)
    1   CONTINUE
        DO 2 I=1,N
        AMF(I)=AMX(I)/TOT
    2   CONTINUE
        RETURN
        END


C**********************************************************************
C        THIS FUNCTION CALCULATES THE RATE CONSTANT FOR THE
C        DESULFURISATION REACTION AS A FUNCTION OF TEMPERATURE.
C**********************************************************************
        FUNCTION RATCON(T)
        RATCON=5.8E+12*EXP(-18118./T)
        RETURN
        END
```

```
C*********************************************************************
C          THIS FUNCTION SUBPROGRAM CALCULATES THE IDEAL SPECIFIC HEATS
C          VALUES FOR HYDROGEN AND METHANE AS A FUNCTION OF TEMPERATURE
C*********************************************************************
          FUNCTION CP(TEM,I)
          GO TO (1,2,3,4,5) I
    1     CP=6.52+.78E-03*TEM+.12E-05*TEM**-2
          RETURN
    2     CP=3.381+18.044E-03*TEM-4.3E-06*TEM**2
          RETURN
    3     CP=7.81+2.96E-03*TEM-.46E-05*TEM**-2
          RETURN
    4     CP=2.247+38.201E-03*TEM-11.049E-06*TEM**2
          RETURN
    5     CP=2.410+57.195E-03*TEM-17.533E-06*TEM**2
          RETURN
          END
```

APPENDIX - D

PROGRAM DESCRIPTION FOR THE DIESEL HYDROTREATER MODEL

1)USAGE

The program computes the sulfur concentration, temperature, molar flow rate, fraction of feed hydrocracked and hydrogen consumption at the exit of the reactor. The main program uses the subroutines DGIL along with other subroutines such as MIXHY, INTRCT to solve the model equations. There are altogether 11 subroutines all of which are written in Fortran IV.

2)SUBROUTINES REQUIRED

SUBROUTINE DGIL: This subroutine solves the differential energy and material balance equations using the Runge-Kutta-Gill method.

SUBROUTINE PROP: (same as in Appendix A)

SUBROUTINE ENTHL: This subroutine calculates the enthalpy of the liquid and vapour phase based on the Peng-Robinson's EOS.

SUBROUTINE NEWRAP: This subroutine solves the non-linear equation for flash calculation to estimate the V/L ratio as well as the liquid and vapour composition.

SUBROUTINE PHILN: This subroutine calculates the fugacity coefficient based on the Peng-Robinson's EOS.

SUBROUTINE CUBEQ: (same as in Appendix A)

SUBROUTINE VAPRES: This subroutine calculates the ideal vapour-liquid equilibrium ratio at reaction conditions

SUBROUTINE MOLAV: This subroutine calculates the average molecular weight of

a mixture.

SUBROUTINE MFRAC: This subroutine calculates the mole fraction of the components from the molar flow rate.

SUBROUTINE MIXHY: This subroutine calculates the critical properties of the hydrogen gas mixture.

SUBROUTINE INTRCT: This subroutine calculates the interaction parameter required for calculating the critical properties of the hydrogen gas mixture.

FUNCTION RATCON: This function subprogram calculates the reaction rate constant for the desulfurisation reaction.

FUNCTION RATCR: This function subprogram calculates the specific rate constant for the hydrocracking reaction.

FUNCTION CP: This function subprogram calculates the ideal gas heat capacity of the different components in the hydrogen gas mixture.

2) DESCRIPTION OF THE PARAMETERS

MAIN:

TC1,VC1, PC1   critical temperature, critical volume and critical pressure of the hydrogen gas mixture.

OM1,AML   acentric factor and molecular weight of the hydrogen gas mixture

HRCR   heat of reaction for the hydrocracking reaction, kcal/kmol

YS   mass fraction sulfur in liquid feed at reactor inlet

YSØ   mass fraction sulfur in liquid reaction mixture at the exit of the reactor

CS   mass/mol fraction sulfur in liquid feed at reactor inlet

CSØ   mol fraction sulfur in liquid reaction mixture

WH   mass flow rate of the hydrogen gas mixture , kg/h

HMOL   molecular weight of the hydrogen gas mixture

FMF   mole fraction of the pseudo-components and the hydrogen gas mixture based on the total molar flow rate of the reaction mixture.

BK   vapour-liquid equilibrium ratio

XL,XV   molar liquid and vapour compositions

X1   vapour to feed ratio

AVM,AVM1   average molecular weight of the vapour and liquid respectively

VAP,LIQ   molar flow rate of the vapour and liquid respectively, kmol/h

WCON   mass fraction of the uncracked feed

SUBROUTINE DGIL:

FMF1   mass fraction of the components including hydrogen gas mixture

CSØ   mole fraction of sulfur in the liquid phase

SHTRX   heat of reaction for the HDS reaction, kcal/kmol S

SGØ   specific gravity of the pseudo-components

WHØ   mass flow rate of the hydrogen gas mixture, kg/h

HRCRØ   heat of reaction for the hydrocracking reaction, kcal/mol

CRØ   mol fraction of the feed left uncracked in the liquid phase

ALIQ,VAP   liquid and vapour molar flow rate, kmol/h

XL,YV   molar concentration of the liquid and vapour phase

RATIO   vapour to liquid mole ratio

WCR   mass of the feed hydrocracked, kg/h

STP	pressure drop per integration step, atm
AB	molar flow rate of the gas mixture, kmol/h
HMOL	molecular weight of the hydrogen gas mixture
AVML	average molecular weight of the liquid feed
D1,D1R	change in the molar concentration of sulfur and uncracked feed
EX	increase in the number of moles in the liquid phase due to hydrocracking
ENTVAP	enthalpy of the vapour phase, kcal/kmol
ENTLIQ	enthalpy of the liquid phase, kcal/kmol
FMCPØ	$\Sigma(mole)_i(sp.\ heat)_i$, kcal/K
DCOH	$\Sigma(-\Delta H_R)'k_i y_i$
DCE	$=dT/dW$
VPRØ	vapour pressure of the different pseudo-components at reaction conditions

SUBROUTINE PROP:(same as in Appendix A)

SUBROUTINE ENTHL:(parameter description is same as in Appendix C)

SUBROUTINE NEWRAP:

VFRAC	vapour to feed mole ratio
XF	molar concentration of the feed
BK	vapour to liquid equilibrium ratio
N	total number of components
XL	molar concentration of the liquid phase
Y	molar concentration of the vapour phase
PT	pressure at which V/F has to be calculated
T	temperature at which the V/F has to be calculated

SUBROUTINE PHILN: (same as in Appendix A)

SUBROUTINE CUBEQ: (same as in Appendix A)

SUBROUTINE VAPRES:

T   reaction temperature, K

TC   critical temperature of the pseudo-components, K

OMEGA   acentric factor

VPR   reduced vapour pressure

N   number of components

PT   reactor pressure, atm

BK   vapour- liquid equilibrium ratio

PC   critical pressure, atm

FØ,F1   parameters in Lee-Kesler's modification of Pitzer's equation.

SUBROUTINE MOLAV:

AMOL   molecular weight of the components

XL   molar concentration of the components

N   total number of components

AVM   average molecular weight

SUBROUTINE MFRAC:(same as in Appendix C)

SUBROUTINE MIXHY: (same as in Appendix C)

SUBROUTINE INTRCT: (same as in Appendix C)

FUNCTION RATCON:

RATCON   specific rate constant for the HDS reaction

FUNCTION RATCR:

RATCR   specific rate constant for the hydrocracking reaction

FUNCTION CP: (same as in Appendix C)

3) DIMENSION REQUIREMENTS

The DIMENSION of different parameters in the MAIN program as well as the subroutines are given in terms of N (total number of pseudo-components) and NC (total number of components in the gas mixture).

MAIN

DIMENSION   CC(N),V(N),TB(N),SG(N),FM(N),OMEGA(N+1),PC(N+1)

TC(N+1),AMOL(N+1),VC(N+1),FMF(N+1),AFM(N),VPR(N)

BK(N+1),XL(N+1),YV(N+1),CF(N),PCX(NC),TCX(NC),VCX(NC)

OMX(NC),AMX(NC),AMF(NC),AMOX(NC),GAMA(NC,NC)

SUBROUTINE DGIL

DIMENSION   CCØ(N),TBØ(N),SGØ(N),TCØ(N+1),VCØ(N+1),AMOLØ(N+1)

OMEGA(N+1),A(4),B(4),C(4),FMF1(N+1),PCØ(N+1),XL(N+1),.

YV(N+1),VPRØ(N+1),BK(N+1),AFM(N),PCX(NC),TCX(NC)

VCX(NC),OMX(NC),AMX(NC),AMF(NC),AMOX(NC)

SUBROUTINE PROP:. (same as in Appendix A)

SUBROUTINE ENTHL: (same as in Appendix C)

SUBROUTINE NEWRAP:

DIMENSION   XF(N+1),BK(N+1),XL(N+1),Y(N+1),TC(N+1),PC(N+1)

OMEGA(N+1)

SUBROUTINE PHILN: (same as in Appendix C)

SUBROUTINE CUBEQ: (same as in Appendix C)

SUBROUTINE VAPRES:

DIMENSION   TR(N),TC(N),OMEGA(N),VPR(N),BK(N),PC(N)

SUBROUTINE MOLAV:

DIMENSION   AMOL(N+1),XL(N+1)

SUBROUTINE MFRAC: (same as in Appendix C)

SUBROUTINE MIXHY: (same as in Appendix C)

SUBROUTINE INTRCT: (same as in Appendix C)

5) INPUTS TO BE SUPPLIED

1) Total number of pseudo-components

2) Total number of components in the hydrogen gas mixture

3) Either the purity of the hydrogen gas mixture or the   detailed

composition.

4) Mid-boiling points of the pseudo-components, ^{o}C

5) Specific gravity of the pseudo-components

6) Total volumetric feed rate, m^3/h

7) Volumetric composition of the feed

8) Average density of the feed, kg/m^3

9) Density of the catalyst bed, kg/m^3

10) Critical properties and the molecular weights of the components
    in the gas mixture

11) Reactor inlet temperature (K) and pressure (atm)

12) Mass fraction sulfur in feed

13) Volumetric flow rate of the recycle and make-up gas, Nm^3/h

14) Volume of catalyst per bed, m^3

15) Total number of beds

16) Number of integration steps per bed

17) Intial guess for vapour to liquid ratio

```
C******************************************************************
C          PROGRAM FOR MODELING OF  DIESEL HYDROTREATER
C
C******************************************************************
          DIMENSION CC(25),V(25),TB(25),SG(25),FM(25),OMEGA(25)
     1    ,PC(25),TC(25),AMOL(25),VC(25),FMA(25),FMF(25),AFM(25),VPR(25)
     1    ,BK(25),XL(25),YV(25),CF(25),PCX(5),TCX(5),
     1    VCX(5),OMX(5),AMX(5),AMF(5),AMOX(5),GAMA(5,5)
          COMMON TOTMOL,X1,WCR,STP,HTOT,AFM,HMOL,GAMA,AVM,PTOT
          COMMON /AREA1/TCX,PCX,VCX,OMX,NC
          OPEN(UNIT=22,DEVICE='DSK',FILE='DIS.IN')
          READ(22,*) (TB(I),I=1,13)
          READ(22,*) (SG(I),I=1,13)
          READ(22,*) (V(I),I=1,13)
          N=13
          NC=5
          TEM=613.
C         TEM=608.
C         TEM=623.
          TCX(1)=41.2;TCX(3)=373.2;TCX(2)=190.6;TCX(4)=305.4
          TCX(5)=369.8
          VCX(1)=65.;VCX(3)=98.5;VCX(2)=99.;VCX(4)=148.;VCX(5)=203.
          PCX(1)=20.8;PCX(3)=88.2;PCX(2)=45.4;PCX(4)=48.2;PCX(5)=41.9
          OMX(1)=0.;OMX(3)=.1;OMX(2)=.008;OMX(4)=.098;OMX(5)=.152
          AMOX(1)=2.;AMOX(3)=34.;AMOX(2)=16.;AMOX(4)=30.;AMOX(5)=44.
C         ***********************************************************
C         JU=1 FOR SET A
C         ***********************************************************
          JU=2
          IF(JU.EQ.1)GO TO 14
C         PURRY=.9;PURMK=.9
C         PURRY=.56;PURMK=.58
          PURRY=.8;PURMK=.86
C         REC=3100.;AMKUP=1500.
C         REC=7200.;AMKUP=2500.
          REC=2900.;AMKUP=1525.
          VH=REC+AMKUP
          AMIX=REC*PURRY+AMKUP*PURMK
          AMX(1)=1000.*AMIX/(82.06*273.)
          AMX(2)=(VH-AMIX)*1000./(82.06*273.)
          CALL MFRAC(AMX,AMF,NC)
          IF(JU.NE.1) GO TO 16
C         ***********************************************************
C         FOR SET A THE MOLAR CONCENTRATION OF THE GAS AT THE
C         REACTOR INLET WAS  KNOWN HENCE MFRAC IS NOT  CALLED
C         ***********************************************************
   14     AMF(1)=.6728;AMF(3)=.01767;AMF(2)=.28499;AMF(4)=.02065
          AMF(5)=3.885E-03
   16     CPM=0.
          DO 5 I=1,NC
          K=I
          CPM=CPM+AMF(I)*CP(TEM,K)
    5     CONTINUE
          CALL INTRCT(GAMA,5)
          CALL MIXHY(AMF,AMOX,TC1,PC1,OM1,VC1,AML,GAMA)
          TC(N+1)=TC1;PC(N+1)=PC1;VC(N+1)=VC1;OMEGA(N+1)=OM1;AMOL(N+1)=AML
          RHOH=AMOL(N+1)*1000./(82.06*273.)
```

```
C         WH=VH*RHOH
C         WH=3060.
          HTOT=WH/AMOL(N+1)
          IF(JU.NE.1) GO TO 15
          DO 89 I=1,NC
          AMX(I)=AMF(I)*HTOT
   89     CONTINUE
   15     CALL PROP(TB,SG,N,TC,PC,VC,AMOL,OMEGA)
          DO 13 I=1,N
          CF(I)=((TB(I)*9./5.)+492.)**(1./3.)/SG(I)
   13     CONTINUE
C         PT=37.
C         STP=.1
          PT=35.
          CALL VAPRES(TEM,TC,OMEGA,VPR,N,PT,BK,PC)
C         BULK DENSITY=45 LBS/FT**3
          RHOB=721.
          RHOF=840.
          SUM=0.
          FT=34.5
C         FT=37.3
C         FT=29.4
          SUMF=RHOF*FT
C         SUMF=26067.
          DO 40 I=1,N
          FM(I)=V(I)*SG(I)*1000./AMOL(I)
          SUM=SUM+FM(I)
   40     CONTINUE
          DO 50 I=1,N
          CC(I)=FM(I)/SUM
   50     CONTINUE
          AVMOL=0.
          DO 10 I=1,N
          AVMOL=AVMOL+CC(I)*AMOL(I)
   10     CONTINUE
          PTOT=SUMF/AVMOL
          TOTMOL=PTOT+HTOT
          HRCR=10000.
          SHTRX=44521.
          CS=.0146
C         CS=.012
C         CS=.0148
C         CS=.02
          YS=CS
          CR=1.
          CR0=CR
          TOTALS=SUMF*CS
          HMOL=AMOL(N+1)
          WRITE(63,27) TOTMOL
   27     FORMAT(2X,'TOTAL NO. OF MOLES AT THE INLET=',F8.2/)
          DO 82 I=1,N
          AFM(I)=CC(I)*PTOT
          FMF(I)=AFM(I)/TOTMOL
   82     CONTINUE
          FMF(N+1)=HTOT/TOTMOL
          BK(N+1)=20.
          X1=.3
```

```
          CALL NEWRAP(X1,FMF,BK,N+1,XL,YV,PT,TEM,TC,PC,OMEGA)
          WRITE(63,2) X1
   2      FORMAT(3X,'V/F RATIO=',F6.4/)
          CALL MOLAV(AMOL,AVM,XL,N+1)
          CALL MOLAV(AMOL,AVM1,YV,N+1)
          WRITE(63,8) AVM,AVM1
   8      FORMAT(3X,'AV. MOL. WT.OF LIQ=',F6.2,'AV. MOL. WT. OF VAP=',F6.
   1      2/)
          VAP=X1*TOTMOL;ALIQ=TOTMOL*(1-X1)
          CS=TOTALS/(ALIQ*32.)
          CSØ=CS
C*******************************************************************
C         N1=NO. OF BEDS
C         N2=NO OF STEPS
C         WCAT=WEIGHT OF CATALYST BED
C*******************************************************************
          N1=1
          N2=25
          VCAT=10.
          WCAT=VCAT*RHOB
          TOTCAT=0.
          DO 69 I=1,N1
          TOTCAT=TOTCAT+WCAT
          CALL DGIL(FMF,CSØ,N,WCAT,N2,TEM,RHOB,TB,SUMF,T2,SHTRX,
   1      SG,WH,TC,VC,AMOL,OMEGA,PC,PT,HRCR,CRØ,ALIQ,VAP,XL,YV
   1      ,AMX,AMOX,CPM)
          YSØ=CSØ*ALIQ*32./SUMF
          WCON=1.-WCR/SUMF
          WRITE (63,4) X1,YSØ,WCON
   4      FORMAT(3X,'V/F RATIO AT THE EXIT=',F6.4,'SULFUR MASS FRAC.='
   1      ,F6.5,'UNCRACK=',F6.5/)
          WRITE(63,28) TOTMOL
  28      FORMAT(3X,'TOTAL NO. OF MOLES AT THE EXIT=',F8.2/)
  30      WRITE(63,45) T2,YSØ,I
  45      FORMAT(4X,'OUTLET TEMP=',F6.2,'K',2X,
   1      'OUTLET SULFUR CONC=',F6.4,2X,'BED NUMBER=',I2//)
          IF(I.EQ.3) GO TO 35
  69      CONTINUE
  35      HCON=(YS-YSØ)*6./32.*SUMF+WCR*2./AVMOL
          WRITE(63,46) HCON
  46      FORMAT(4X,'H2 CONSUMED=',F8.2,'KG'//)
          STOP
          END



C*******************************************************************
C         THIS SUBROUTINE USES THE RUNGE - KUTTA - GILL METHOD TO
C         NUMERICALLY INTEGRATE THE DIFFERENTIAL MASS AND ENERGY
C         EQUATIONS.
C*******************************************************************
          SUBROUTINE DGIL(FMF1,CSØ,NØ,WCATØ,N2Ø,TEMØ,RHOB,TBØ,
   1      SUMFØ,T2Ø,SHTRX,SGØ,WHØ,TCØ,VCØ,AMOLØ,OMEGA,PCØ,PTØ
   1      ,HRCRØ,CRØ,ALIQ,VAP,XL,YV,AMX,AMOX,CPM)
          COMMON TOTMOL,RATIO,WCR,STP,AB,AFM,HMOL,GAMA,AVML,PTOT
          COMMON /AREA1/TCX,PCX,VCX,OMX,NC
          DIMENSION TBØ(25),SGØ(25),TCØ(25),VCØ(25),AMOLØ(25)
   1      ,OMEGA(25),A(4),B(4),C(4),FMF1(25),PCØ(25),XL(25),YV(25)
```

```
1    ,VPRØ(25),BK(25),AFM(25),PCX(5),TCX(5),VCX(5),OMX(5
1    ),AMX(5),AMF(5),AMOX(5),GAMA(5,5)
     BK(NØ+1)=20.
     X=Ø.
     X1=1.
     N1=1
     H=(X1-X)/(FLOAT(N2Ø))
     D6=H*.5
     X=X+D6
     QQ=Ø.
     Q=Ø.
     QR=Ø.
     A(1)=.5
     B(1)=2.
     C(1)=.5
     A(2)=1.-SQRT(.5)
     B(2)=1.
     C(2)=A(2)
     A(3)=1.+SQRT(.5)
     B(3)=1.
     C(3)=A(3)
     A(4)=1./6.
     B(4)=2.
     C(4)=.5
     CALL ENTHL(TCØ,PCØ,OMEGA,PTØ,TEMØ,XL,ENTLIQ,SGØ,TBØ,NØ+1,AMOLØ,1
1    ,CPM)
     CPL=ENTLIQ/(TEMØ-273.)
4    DO 3 J=1,4
     CPM=Ø.
     DO 16 I=1,NC
     K=I
     CPM=CPM+AMF(I)*CP(TEMØ,K)
16   CONTINUE
     CALL ENTHL(TCØ,PCØ,OMEGA,PTØ,TEMØ,YV,ENTVAP,SGØ,TBØ,NØ+1,AMOLØ
1    ,2,CPM)
     CPV=ENTVAP/(TEMØ-273.)
     DC=-RATCON(TEMØ)*(CSØ**2)
     DCR=-RATCR(TEMØ)*CRØ
     DCM=DC*WCATØ/ALIQ
     DCMR=DCR*WCATØ/ALIQ
     DCOH=SHTRX*RATCON(TEMØ)*(CSØ**2)+HRCRØ*RATCR(TEMØ)*CRØ
     HFRTØ=DCOH+HFRTØ
     D=A(J)*(DCM-B(J)*Q)
     DR=A(J)*(DCMR-B(J)*QR)
     D1=H*D
     D1R=H*DR
     AMX(1)=AMX(1)+D1*ALIQ*3+D1R*ALIQ
     AMX(3)=AMX(3)-D1*ALIQ
     CALL MFRAC(AMX,AMF,NC)
     CALL MIXHY(AMF,AMOX,TC1,PC1,OM1,VC1,AML,GAMA)
     TCØ(NØ+1)=TC1;PCØ(NØ+1)=PC1;VCØ(NØ+1)=VC1;OMEGA(NØ+1)=OM1
     AMOLØ(NØ+1)=AML
     XTOT=Ø.
     DO 7Ø I=1,NC
     XTOT=XTOT+AMX(I)*AMOX(I)
7Ø   CONTINUE
     AB=XTOT/AMOLØ(NØ+1)
```

```
        TOTMOL=PTOT+AB
        WCR=WCR-D1R*ALIQ*AVML
        CSØ=CSØ+D1
        CRØ=CRØ+D1R
        D2=D*3.
        D2R=DR*3.
        D3=C(J)*DCM
        D3R=C(J)*DCMR
        D2=D2-D3
        D2R=D2R-D3R
        Q=Q+D2
        QR=QR+D2R
        FMCPØ=VAP*CPV+ALIQ*CPL
        DCE=DCOH*WCATØ/FMCPØ
        DD=A(J)*(DCE-B(J)*QQ)
        DD1=H*DD
        TEMØ=TEMØ+DD1
        DD2=DD*3.
        DD3=C(J)*DCE
        DD2=DD2-DD3
        QQ=QQ+DD2
        IF(J.GT.1) GO TO 2
        GO TO 7
  2     IF(J.GT.2) GO TO 7
        X=X+D6
  7     RATIO=.8
        AFM(NØ+1)=AB
        DO 9 I=1,NØ
        FMF1(I)=AFM(I)/TOTMOL
  9     CONTINUE
        FMF1(NØ+1)=AB/TOTMOL
        CALL VAPRES(TEMØ,TCØ,OMEGA,VPRØ,NØ,PTØ,BK,PCØ)
        CALL NEWRAP(RATIO,FMF1,BK,NØ+1,XL,YV,PTØ,TEMØ,TCØ,PCØ,OMEGA)
        CALL MOLAV(AMOLØ,AVML,XL,NØ+1)
        CALL MOLAV(AMOLØ,AVMV,YV,NØ+1)
        VAP=RATIO*TOTMOL
        YSØ=CSØ*32.*ALIQ/SUMFØ
        CS1=CSØ
        AL1=ALIQ
        CSØ=CSØ*AL1/(TOTMOL*(1.-RATIO))
        YRØ=(1.-WCR/SUMFØ)
        CR1=CRØ
        CRØ=CR1*TOTMOL*(1.-RATIO)/AL1
        ALIQ=TOTMOL*(1.-RATIO)
  3     CONTINUE
        WRITE(63,48) N1,X,TEMØ,YSØ,YRØ
 48     FORMAT (2X,'STEP NO.=',I3,2X,'FRACT. WEIGHT OF THE BED=',
     1  F4.2,2X,'TEMPERATURE=',F7.2,'K',2X,'SULFUR CONC.=',F6.5,2X,'
     1  UNCRACKED CONC.=',F6.4//)
        IF(N1.EQ.N2)GO TO 5
        PTØ=PTØ-STP
        N1=N1+1
        IF(X.GT.X1) GO TO 5
        X=X+D6
        RATIO=.8
        CALL VAPRES(TEMØ,TCØ,OMEGA,VPRØ,NØ,PTØ,BK,PCØ)
        CALL NEWRAP(RATIO,FMF1,BK,NØ+1,XL,YV,PTØ,TEMØ,TCØ,PCØ,OMEGA)
```

```
          CALL MOLAV(AMOLØ,AVML,XL,NØ+1)
          CALL MOLAV(AMOLØ,AVMV,YV,NØ+1)
          VAP=RATIO*TOTMOL
          CSØ=CS1*AL1/(TOTMOL*(1.-RATIO))
          CRØ=CR1*TOTMOL*(1.-RATIO)/AL1
          ALIQ=TOTMOL*(1.-RATIO)
          GO TO 4
    5     T2Ø=TEMØ
          WRITE(63,22) AVML,AVMV
   22     FORMAT(3X,'VAP AVERAGE MOL.WT.=',F6.2,'LIQ AVERAGE MOLWT.=',
    1     F6.2)
          RETURN
          END


C***************************************************************
          SUBROUTINE PROP   (same as in Appendix A)
C***************************************************************


C***************************************************************
C         THIS SUBROUTINE ESTIMATES THE ENTHALPY OF THE LIQUID AND
C         VAPOUR PHASE BASED ON THE PENG-ROBINSON'S EQUATION OF STATE.
C***************************************************************
          SUBROUTINE ENTHL(TC,PC,OMEGA,PT,T,Y,ENTH,SG1,TBPP,N,AMW,L1
    1     ,CPM)
          DIMENSION TC(25),PC(25),OMEGA(25),Y(25),SG1(25),TBPP(25),
    1HILN(26),PHIL1(26),PHI(26),PHI1(26),AMW(25),AK(25),HID(25)
    1,CF(25),CP(25),TBPR(25)
          CALL PHILN(TC,PC,OMEGA,PT,T,Y,HILN,PHI,N,2,L1)
          CALL PHILN(TC,PC,OMEGA,PT,(T*1.ØØØ1),Y,PHIL1,PHI1,N,2,L1)
          HEX=Ø.
          DO 1Ø I=1,N
          HEX=HEX+((PHIL1(I)-HILN(I))*Y(I)/(.ØØØ1*T))
   1Ø     CONTINUE
          R=1.987
          HEX=-R*(T**2)*HEX
          TR=(T-273.)*9./5.+492.
          TF=(T-273.)*9./5.+32.
          HIDL=Ø.
          DO 2Ø I=1,N-1
          HID(I)=215.-87.*SG1(I)+(.415-.1Ø4*SG1(I))*TF+(.ØØØ31Ø-
    1.ØØØØ78*SG1(I))*TF**2
          HIDL=HIDL+Y(I)*AMW(I)*HID(I)*252./453.5
   2Ø     CONTINUE
          HID(N)=CPM*(T-273.)
          HIDL=Y(N)*HID(N)+HIDL
          ENTH=HEX+HIDL
          RETURN
          END


C***************************************************************
C         THIS SUBROUTINE CALCULATES THE FRACTION OF THE FEED IN THE
C         VAPOUR PHASE ASSUMING IDEAL Ki VALUES, GIVEN FEED COMPOSITION
C***************************************************************
          SUBROUTINE NEWRAP(VFRAC,XF,BK,N,XL,Y,PT,T,TC,PC,OMEGA)
          DIMENSION XF(25),BK(25),XL(25),Y(25),TC(25),PC(25),OMEGA(25)
    1     ,BK1(25),HILN1(26),HILN2(26),PHI(26)
   53     VFRAC=.1
```

```
            DVFRAC=.Ø5
            FLAGP=1.
            FLAGM=1.
            LOOP=Ø
    1Ø      LOOP=LOOP+1
            IF(LOOP.GT.1ØØ) STOP
            SUMX=Ø.
            DO 15 J=1,N
            XL(J)=XF(J)/(1.+VFRAC*(BK(J)-1.))
    15      SUMX=SUMX+XL(J)
            IF(ABS(SUMX-1.).LT..ØØØØØ5) GO TO 5Ø
            IF(SUMX-1.)2Ø,2Ø,3Ø
    2Ø      IF(FLAGP)21,21,22
    21      DVFRAC=DVFRAC*.5
    22      VFRAC=VFRAC+DVFRAC
            FLAGM=-1.
            GO TO 1Ø
    3Ø      IF(FLAGM)31,31,32
    31      DVFRAC=DVFRAC*.5
    32      VFRAC=VFRAC-DVFRAC
            FLAGP=-1.
            GO TO 1Ø
    5Ø      DO 51 J=1,N
            Y(J)=XL(J)*BK(J)
    51      SUM2=SUM2+Y(J)
            RETURN
            END


C**************************************************************************
            SUBROUTINE PHILN (same as in Appendix C)
C**************************************************************************

C**************************************************************************
            SUBROUTINE CUBEQ (same as in Appendix A)
C**************************************************************************


C**************************************************************************
C           THIS SUBROUTINE ESTIMATES THE VAPOUR PRESSURE AS A FUNCTION
C           OF TEMPERATURE USING LEE-KESLER'S MODIFICATION OF PITZER
C           EQUATION
C**************************************************************************
            SUBROUTINE VAPRES(T,TC,OMEGA,VPR,N,PT,BK,PC)
            DIMENSION TR(25),TC(25),OMEGA(25),VPR(25),BK(25),PC(25)
            DO 1Ø I=1,N
            TR(I)=T/TC(I)
            FØ=5.92714-6.Ø9648/TR(I)-1.28862*ALOG(TR(I))+.169347*TR(I)**6
            F1=15.2518-15.6825/TR(I)-13.4721*ALOG(TR(I))+.43577*TR(I)**6
            VPR(I)=EXP(FØ+OMEGA(I)*F1)
            BK(I)=VPR(I)*PC(I)/PT
    1Ø      CONTINUE
            RETURN
            END


C**************************************************************************
C           THIS SUBROUTINE CALCULATES THE AVERAGE MOLECULAR WEIGHT OF THE
C           GAS OR LIQUID MIXTURE
```

```
C*******************************************************************
        SUBROUTINE MOLAV(AMOL,AVM,XL,N)
        DIMENSION AMOL(25),XL(25)
        AVM=0.
        DO 10 I=1,N
        AVM=AVM+XL(I)*AMOL(I)
 10     CONTINUE
        RETURN
        END

C*******************************************************************
        SUBROUTINE MFRAC (same as in Appendix C)
C*******************************************************************

C*******************************************************************
        SUBROUTINE MIXHY (same as in Appendix C)
C*******************************************************************

C*******************************************************************
        SUBROUTINE INTRCT (same as in Appendix C)
C*******************************************************************

C*******************************************************************
C       THIS FUNCTION SUBPROGRAM ESTIMATES THE RATE CONSTANT FOR THE
C       DESULFURISATION FUNCTION AS A FUNCTION OF TEMPERATURE
C*******************************************************************
        FUNCTION RATCON(T)
        RATCON=9.8E+09*EXP(-15500./T)
C       RATCON=6.5E+09*EXP(-15500./T)
        RETURN
        END

C*******************************************************************
C       THIS FUNCTION ESTIMATES THE RATE CONSTANT FOR THE CRACKING
C       REACTION .
C*******************************************************************
        FUNCTION RATCR(T)
        RATCR=4.E+05*EXP(-13416./T)
        RETURN
        END

C*******************************************************************
        FUNCTION CP (same as in Appendix C)
C*******************************************************************
```